VOL. XXVII 1915

TRANSACTIONS

OF THE

AMERICAN ELECTROCHEMICAL SOCIETY.

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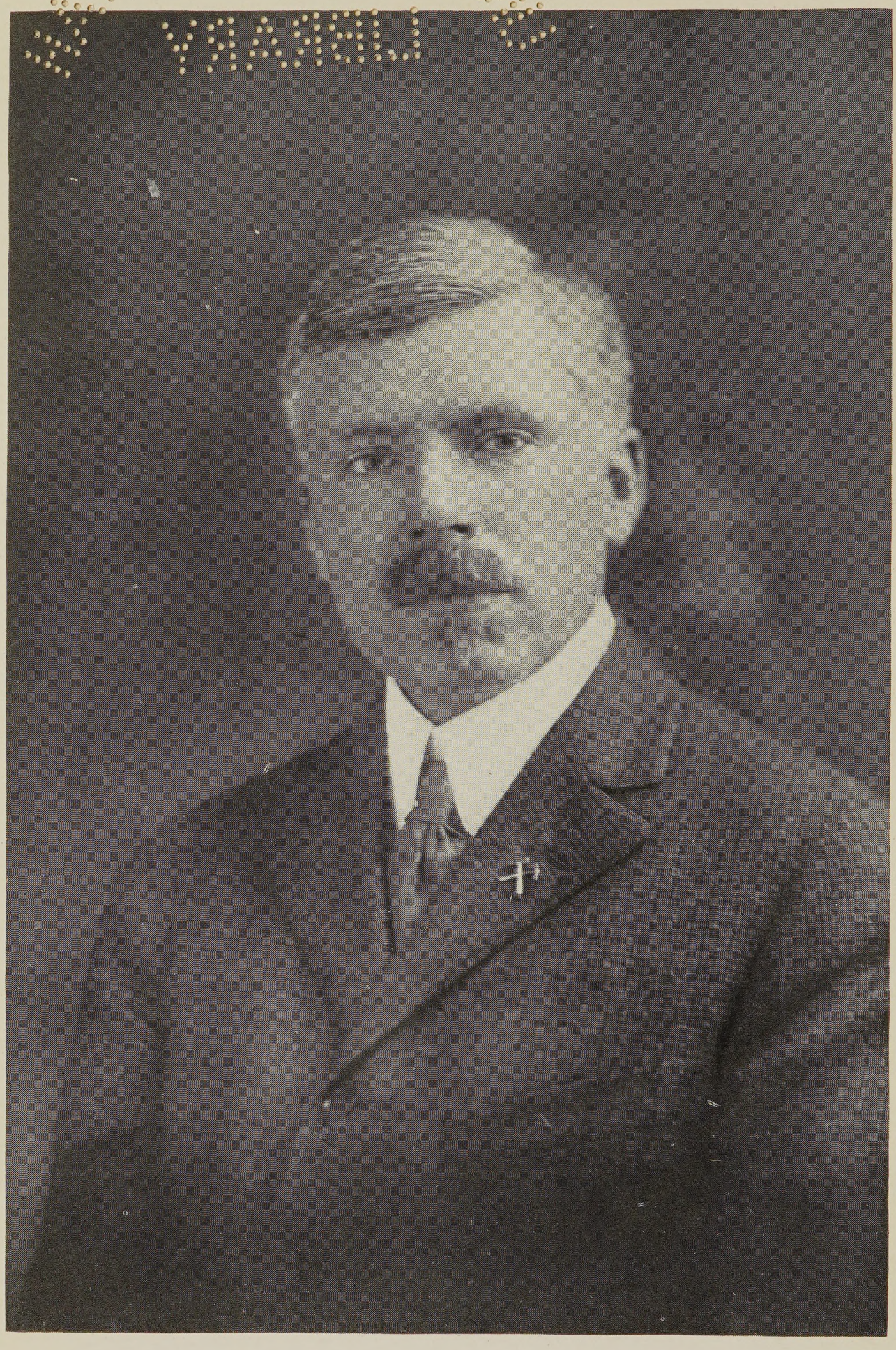

Lawrence Addicks –

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TRANSACTIONS

OF THE

AMERICAN ELECTROCHEMICAL SOCIETY

157568

VOLUME XXVII

TWENTY-SEVENTH GENERAL MEETING

ATLANTIC CITY, APRIL 22, 23, 1915

PHILADELPHIA, APRIL 24, 1915

PUBLISHED BY

THE AMERICAN ELECTROCHEMICAL SOCIETY

AT THE OFFICE OF ITS SECRETARY

LEHIGH UNIVERSITY, SOUTH BETHLEHEM, PA.

1915

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VOLUME XXVII. 1915.

TRANSACTIONS

OF THE

AMERICAN ELECTROCHEMICAL SOCIETY

PROCEEDINGS

CONDENSED MINUTES OF THE TWENTY-SEVENTH GENERAL MEETING OF THE SOCIETY, HELD AT ATLANTIC CITY, N. J., APRIL 22 AND 23, AND IN PHILADELPHIA, PA., APRIL 24, 1915.

Number of members registered, 71; number of guests registered, 60; total, 131.

PROCEEDINGS OF THURSDAY, APRIL 22.

The Publication Committee met at 10.30 A. M., and the Board of Directors at 11 A. M., at the Hotel Chalfonte. The annual report of the Secretary and Treasurer, and other actions there taken aside from routine business, will be found immediately following in these proceedings.

The annual business meeting of the Society was called to order at 2 P. M., in the Convention Hall of the Hotel Chalfonte, F. A. Lidbury, president, in the chair.

The reading of the minutes of the Twenty-sixth General Meeting was dispensed with, they being approved as printed in Volume XXVI of the Transactions.

The report of the Board of Directors, including those of the Secretary and Treasurer, was read by the Secretary, and accepted for publication in the proceedings of the meeting, to which it is appended. These reports show in brief a total membership of 1,377 at the close of 1914, a net gain of 1 during the year. The financial report showed a status which might be considered satisfactory considering prevailing conditions. Receipts had diminished considerably during the year, and the net assets of the

Society at the close of 1914 were: Cash on hand, $492.88; permanent investment, $6,121,11; less outstanding note, $2,000; net assets, $4,613.99.

The report of the Publication Committee was then read by the Secretary, showing that 15 papers had been secured and accepted for the Twenty-sixth General Meeting, and 18 papers and 2 lectures for this the Twenty-seventh General Meeting.

In the absence of the Tellers, the report of the Annual Election of Officers was opened and read by the Secretary.

Report of the Tellers of Election.

To the Members of the American Electrochemical Society:

Gentlemen: Following is a list of the votes cast in the election for officers for the year 1915-16:

President: L. Addicks 199, L. Kahlenberg 1, E. R. Taylor 1, Acheson Smith 1, W. L. Miller 1.

Vice-Presidents: L. E. Saunders 177, J. A. Mathews 163, L. Kahlenberg 129, A. von Isakovicks 46, H. R. Carveth 42, W. L. Miller 31, L. Addicks 4, F. J. Tone 2, C. F. Chandler 1, S. A. Tucker 1, F. A. Lidbury 1.

Managers: L. D. Vorce 134, Acheson Smith 131, W. H. Walker 118, C. F. Burgess 75, L. H. Baekeland 43, F. C. Frary 28, S. A. Tucker 27, C. P. Townsend 22, F. J. Tone 22, W. L. Miller 10, T. F. Baily 4.

Treasurer: P. G. Salom 199.

Secretary: J. W. Richards 203, F. A. J. FitzGerald 2.

Respectfully submitted,

G. A. Roush,
A. S. Callen,
J. Wm. Fehnel.

The Chairman then announced the following elections to office, as the result of the ballots cast:

President (for one year): Lawrence Addicks.

Vice-Presidents (for two years): L. E. Saunders, J. A. Mathews, L. Kahlenberg.

Managers (for three years): L. D. Vorce, Acheson Smith, W. H. Walker.

Treasurer (for one year): Pedro G. Salom.

Secretary (for one year): Joseph W. Richards.

President-elect Addicks was called to act as Chairman *pro tem.* while President Lidbury delivered the Presidential Address, as printed in full in these Transactions.

Reading of papers and discussion were then taken up, papers being presented by the following, and discussed as printed in these Transactions: E. Weintraub, Boyd Dudley, Jr. (presented in abstract by Secretary Richards), O. L. Kowalke and D. S. Grenfell (presented in abstract by F. A. J. FitzGerald).

At 8 P. M. Prof. W. S. Franklin, of Lehigh University, delivered an Experimental Lecture before the Society on "Some Mechanical Analogies of Electrical and Magnetic Phenomena," which was highly interesting and greatly enjoyed by an audience which completely filled the Convention Hall of the Chalfonte.

PROCEEDINGS OF FRIDAY, APRIL 23.

The meeting was called to order at 10 A. M., in the Convention Hall of the Chalfonte, President Lidbury in the Chair. Papers were presented by the following, and discussed as printed in full in these Transactions: W. D. Bancroft (presented in abstract by W. R. Whitney), W. D. Bancroft (presented in abstract by F. C. Frary), T. S. Fuller, M. deK. Thompson and E. C. Crocker (presented by W. F. Gillett), and concluding with a General Discussion on Problems in Copper Leaching, first begun at a session of the New York Section of this Society, January 6, 1915, and continued here by L. Addicks, J. V. N. Dorr, F. C. Frary, J. W. Richards and W. R. Whitney.

The afternoon session was called to order at 2 P. M., in the same Hall. Papers were presented by the following, and discussed as printed in full in these Transactions: F. C. Frary and H. C. Berman (presented by Mr. Frary), W. E. Rieder, L. L. Summers, E. S. Washburn (presented in abstract by C. J. Fink), S. Peacock (presented in abstract by F. A. J. FitzGerald).

PROCEEDINGS OF SATURDAY, APRIL 24.

The meeting was called to order at 9.30 A. M., in the Harrison Chemical Laboratory of the University of Pennsylvania, in Philadelphia, president-elect Addicks in the chair. This session was a Joint Session with the Illuminating Engineering Society.

Papers were read by the following, and discussed as printed in full in these Transactions: H. E. Ives, W. C. Moore (presented by W. R. Mott), R. E. Harrington.

At 12.30 the Society and its guests were handsomely entertained at luncheon in Houston Hall by the authorities of the University of Pennsylvania, represented by Provost Smith.

The afternoon session, a Joint Session with the American Electroplaters' Society, was called to order at 2 P. M., President Lidbury in the chair. Dr. Edgar F. Smith, Provost of the University, and known internationally for his labors on Electroanalysis, delivered an Experimental Lecture on "The Development of Electroanalysis in America." After discussion of the lecture, papers were read by the following, and discussed as printed in full in these Transactions: O. P. Watts (presented in abstract by F. C. Frary), F. C. Mathers and A. McKinney (presented in abstract by Secretary Richards), H. T. Kalmus, C. H. Harper and W. L. Savell (presented in abstract by W. Lash Miller).

The Secretary then presented the following resolution, which was duly seconded and passed:

Mr. President and Gentlemen: "I move a cordial vote of thanks be extended to the authorities of the University of Pennsylvania for their generous hospitality; to Provost Smith and his assistants for their aid in the success of this meeting, and to the Local Committee of the Society for their time and trouble in arranging this most interesting and successful meeting."

President Lidbury then declared the meeting closed.

ANNUAL REPORT OF THE BOARD OF DIRECTORS.

To the Members of the American Electrochemical Society:

We submit herewith the annual reports of the Secretary and Treasurer for the year 1914, the former containing the detailed financial statement of receipts and expenditures.

The net increase in the number of members during the year 1914 was 1, the membership at the end of the year being 1,377; 29 members have been elected since the first of the year; there are 3 applications on file waiting action of the Board.

The financial status of the Society during 1914 was satisfactory considering the prevailing conditions. Membership did not increase, and receipts fell off, but not to such an extent as to embarrass us financially. The loans which had been made in previous years to tide us over the end of the year had to be repeated, and were paid off more slowly in 1915 than in 1914; the Board has authorized the sale of a $1,000 bond, to meet the present financial stringency.

The following are the more important actions taken by the Board of Directors during the past year:

The sum of $50 was appropriated for the current contribution of the Society to the Annual Tables of Physical and Chemical Constants.

The Secretary of the Society was authorized to become a member of the Society of Technical Associations' Secretaries, the $10 annual fee being paid by the Society, on condition that this membership is considered membership for the Society and not personal for the Secretary.

SECRETARY'S ANNUAL REPORT.

To the Board of Directors of the American Electrochemical Society:

GENTLEMEN: In 1914 the Society held two general meetings, one at New York City, April 16, 17 and 18, 1914, at which the attendance was 157 members and 167 guests, total 324; the second at Niagara Falls, October 1, 2 and 3, 1914, at which the attendance was 119 members and 124 guests, total 243. The Transactions of the Spring meeting include 34 papers, and those of the Fall meeting 15 papers.

In 1914 there were issued and distributed to our members two volumes of the Transactions: Volume XXIV, the Transactions of the meeting held in Denver, September 9, 10 and 11, 1913; Volume XXV, of the New York City meeting, April 16, 17 and 18, 1914. These volumes contained 396 and 544 pages respectively.

The Transactions of the Niagara Falls meeting, October 1, 2 and 3, 1914, were issued January 29, 1915, and contained 270 pages.

The edition of the 1914 volumes was 1,500 copies bound in cloth for distribution to our members; 50 extra copies in sheets for distribution in pamphlet form to authors of papers; 250 copies bound in paper for distribution to the Faraday Society; 500 copies sewed, ready for binding, to be kept in stock.

Complete sets of the Transactions are still on hand, but the stock is rapidly diminishing, and Volumes I, II and III will hereafter be sold at double price, according to action of the Board of Directors.

The stock of Volumes on hand December 31, 1914, was as follows:

Volume	Bound in Cloth	Bound in Paper or Stitched Ready for Binding	Total
I	160	12	172
II	189	0	189
III	95	0	95
IV	118	234	352
V	72	234	306
VI	88	239	327
VII	89	247	336
VIII	105	248	353
IX	106	275	381
X	112	257	369
XI	107	267	374
XII	107	266	373
XIII	126	220	346
XIV	236	252	488
XV	229	223	452
XVI	231	290	521
XVII	167	521	688
XVIII	180	522	702
XIX	51	531	582
XX	51	535	586
XXI	52	555	607
XXII	60	548	608
XXIII	52	545	597
XXIV	65	558	623
XXV	121	543	664

Condition of the Society in regard to membership in 1914:

Members January 1, 1914		1,376
Elected and qualified as members in 1914		97
		1,473
Resignations in 1914	38	
Deaths in 1914	9	
Dropped for non-payment of dues	49	
	—	96
Members December 31, 1914		1,377

Financial Statement.

January 1, 1914 to December 31, 1914.

Cash assets beginning January, 1914, account		$119 90

RECEIPTS.

Entrance fees	$470 00	
Current dues	4,629 51	
Advance dues for 1915	1,555 00	
Sales of publications	905 70	
Advertisements	336 47	
Interest on bonds and bank account	308 60	
Rebate on Faraday payment	4 12	
Loans	1,969 00	
		10,178 40
Total		$10,298 30

EXPENDITURES.

Office printing	$463 31	
Express and postage	876 45	
Publications	4,752 44	
Local sections	342 00	
Secretarial appropriation	1,500 00	
Office expenses	352 06	
Office furniture	247 63	
Storage	106 85	
Commission on advertisements	33 65	
Meetings	599 03	
Annual Table of Constants	50 00	
Faraday Society transactions	472 00	
Dues, Society of Technical Association Secretaries	10 00	
		9,805 42
Cash Balance, beginning January, 1915, account		$492 88

ASSETS, JANUARY 1, 1914.

Cash balance, January 1, 1914:	
On deposit	$69 90
Cash box	50 00
Bonds held by Society (cost price)	6,121 11
	$6,241 01

ASSETS, DECEMBER 31, 1914.

Cash balance, December 31, 1914:	
On deposit	$442.88
Cash box	50 00
Bonds held by Society (cost price)	6,121 11
	$6,613.99
Less outstanding note to E. P. Wilbur Trust Co.	2,000 00
	$4,613 99

Jos. W. Richards, *Secretary.*

TREASURER'S ANNUAL REPORT.

FOR THE YEAR 1914.

Jan. 1.	Cash balance	$119 90	
Jan. 1 to Dec. 31.			
	Receipts as per statement attached	10,178 40	
	Total receipts	10,298 30	
	Expenditures, 1914, as per statement attached	9,805 42	
	Balance, Dec. 31, 1914		492 88
Dec. 31.	Balance, E. P. Wilbur Trust Co.	1,782 89	
	Less checks not presented	1,348 67	
		434 22	
	Balance, Commonwealth T. I. & T. Co.	8 66	
	Balance in cash drawer	50 00	
			$492 88

P. G. Salom, *Treasurer.*

We have examined the above statement of account and receipts and expenditures for the year 1914 and find the same to be correct.

We also report $3,000 Philadelphia Electric Company gold trust certificates, and receipt from Jos. W. Richards for $3,000 U. S. Steel Corporation bonds used as collateral for loan, in the box of the Society in the safe deposit vaults of the Commonwealth Title Insurance and Trust Company.

S. S. Sadtler,
Carl Hering, } *Auditors.*

ABSTRACT OF MINUTES OF THE BOARD OF DIRECTORS APRIL 22, 1915

The meeting was held April 22, 1915, at 11.30 A. M., in the Convention Hall of the Chalfonte Hotel, Atlantic City.

Present in person: President Lidbury, Roeber, Hering, Addicks, Saunders, FitzGerald, Schluederberg, Fink and Secretary Richards, President Lidbury presiding. Present by proxy: Burgess, Tucker, Townsend, Bancroft, Brady, Kahlenberg, Parmelee, Brown, Whitney and Salom.

The minutes of the meeting of March 26 were approved as printed.

The Secretary reporting that the printed copies of the Constitution were exhausted, it was ordered that the Constitution and By-Laws be reprinted in pocket form, similar in size to the program of the meeting, with such other information regarding the Society as the Secretary considers expedient to include.

It was moved and carried that an appropriation of $50.00 be made to the Committee publishing the Annual Tables of Physical and Chemical Constants.

The Secretary was authorized to change the form of badge used at the meetings, omitting the ribbon and using a permanent form with place for name and a pendant similar to the official Society pin, providing that the change will not be materially more expensive than the present badges.

It was moved and carried that a financial committee of the Board be appointed, consisting of three members, including President Lidbury and Secretary Richards and the appointment of the third member be left to the next President, which committee shall analyze the financial status of the Society and make recommendation to the Board.

It was moved and carried that the Faraday Society be notified that the arrangement for exchanging Transactions will be terminated January 1, 1916, and the Secretary was instructed to see whether special arrangements could be made by which individual members of each Society desiring the Transactions of the other could obtain them at reduced prices.

The Secretary was authorized to sell to libraries only past volumes of the Transactions for $1.00, except Volumes I, II

and III, which are $2.00 per volume, these prices to stand until annulled by the Board.

It was moved and carried that the Treasurer be authorized to sell a $1,000 bond, in order to increase the cash balance of the Society, and enable it to pay bills due.

The report of the Publication Committee was received and accepted, reading as follows:

"During its term of office the present Publication Committee has passed on 40 papers with the following results: Accepted, 21; accepted in modified form, 9; rejected in present form, 2; withdrawn, 1; rejected, 7; total, 40."

The report of the Membership Committee, made verbally by Mr. Addicks, was received and accepted.

The report of the Patent Committee by Dr. L. H. Baekeland was accepted, with thanks for the good work done by the Committee. It read as follows:

"Your Committee on Patents begs to report that it has continued to follow with careful interest any events relating to the patent laws of this country, with the object of aiding in abolishing present defects and to favor constructive legislation which may bring our patent laws in harmony with the modern growth of our industries. Unfortunately, there seems to exist just now, on the part of some of our legislators, a tendency towards destructive patent legislation. This tendency is mainly the result of lack of good information on the intricate subject of the practical working of patent laws. More than once this unfortunate ignorance of our legislative bodies has had for effect that bills have been introduced which, if passed, would have caused untold harm to our pioneering industries, and to intellectual property in general.

"The members of your committee in every instance have used their best personal effort to prevent such a serious mistake, and to educate legislators as well as the public to the real needs of our patent system.

"Just now it is deemed advisable to wait for awhile until more propitious times, when a systematic effort towards sane and constructive patent reform can be undertaken with more hope of success.

"In the meantime, your committee has kept itself well prepared to co-operate with the other technical organizations of this country to take such opportunistic action as will be warranted by future events."

The report of the Committee on Co-operation with the American Electroplaters' Society, communicated by Chairman Bancroft, was received and the Committee continued. It reads as follows:

"F. C. Mathers has studied the behavior of many nickel baths and silver baths but is not yet ready to report. In the nickel baths he finds that the effect of boric acid is specific and is not due to its being a weak acid. F. C. Frary has measured single potentials and is not ready to report."

A progress report was received from the Committee on Uranium Poisoning and the committee continued.

The report of the Committee on Co-operation with the Electrical Congress was received from Chas. Doremus, stating that the Congress would not be held and asking that the committee be discharged; the committee was therefore discharged.

Jos. W. Richards,
Secretary.

MEMBERS AND GUESTS REGISTERED AT THE TWENTY-SEVENTH GENERAL MEETING.

Members.

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Walter Arthur
L. H. Baekeland
S. D. Benoliel
E. Blough
P. A. Boeck
deCourcy Browne
A. S. Callen
W. R. Clymer
H. B. Coho
K. F. Cooper
Wm. A. Cowan
J. S. Crider
N. E. Dabolt
J. V. N. Dorr
J. Wm. Fehnel
C. G. Fink
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W. S. Franklin
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H. G. Kleinfeldt
F. T. Letchfield
F. A. Lidbury
Chas. F. Lindsay
Hiram S. Lukens
J. Y. McConnell
W. Lash Miller
H. S. Miner
Wm. R. Mott
J. M. Muir
E. F. Northrup
N. Petinot
Chas. H. Procter
Jos. W. Richards
E. G. Rippel
E. F. Roeber
L. E. Saunders
Carl G. Schluederberg
E. M. Sergeant
C. E. Skinner
Acheson Smith
W. M. Snow
L. L. Summers
W. T. Taggart
J. Takamine
F. J. Tone
G. D. VanArsdale
L. D. Vorce
E. Weintraub
W. R. Whitney
A. M. Williamson
C. A. Winder
Chas. Wirt
T. A. Witherspoon
F. C. Woodside
J. A. Yunck

Guests.

Mrs. Lawrence Addicks, Douglas, Ariz.
Wm. H. Adolph, Philadelphia.
T. R. Alexander, Jr., Philadelphia.
Samuel Barr, Philadelphia.
Geo. S. Barrows, Philadelphia
E. H. Bedell, New York City.
Wm. J. Bell, Philadelphia.
Wm. Blum, Washington, D. C.
M. T. Bogert, New York City.
A. T. Borbeck, Philadelphia.
H. C. Chapin, Cleveland, Ohio.

Guests (Continued).

Mrs. deCourcy Browne, New York City.
Mrs. W. R. Clymer, Cleveland, O.
Mrs. H. B. Coho, Mt. Vernon, N. Y.
W. N. Coller, New York City.
S. F. Cox, Princeton, N. J.
Mrs. J. S. Crider, Cleveland, Ohio
R. A. Crider, Cleveland, Ohio.
T. E. Crossman, New York City.
J. L. Dinan, Philadelphia.
C. Dittmar, New York City.
J H. Dorricott, Philadelphia.
H. M. Engle, Marietta, Pa.
G S. Ettla, Philadelphia.
Mrs. F. A. J. FitzGerald, Niagara Falls, N. Y.
H. J. Flanigan, Mt. Vernon, N. Y.
T. S. Fuller, Schenectady, N. Y.
Mrs. W. T. Gibbs, Buckingham, Quebec, Canada.
Miss Mabel E. Gibbs, Buckingham, Quebec, Canada.
R. E. Harrington, Newark, N. J.
E. G. Henderson, Windsor, Ont., Canada.
August Heck, Philadelphia.
J. B. Hill, Philadelphia.
C. A. Holkesvig, Gibbsboro, N. J.
Mrs. W. F. Hubley, East Orange, New Jersey.
Miss Emlen Hubley, East Orange, New Jersey.
H. E. Ives, Philadelphia.
J. E. Johnson, Jr., New York City.
Roy Kegerreis, Philadelphia.
Mrs. H. W. Kellogg, Niagara Falls, N. Y.
Milton Kutz, Philadelphia.
Edw. W. Lawler, Bayonne, N. J.
John H. Müller, Philadelphia.
Wm. Petinot, New York City.
H S. Roberts, 2d, Philadelphia.
W. E. Ruder, Schenectady, N. Y.
Quin Seiber, Philadelphia.
Mrs. E. M. Sergeant, Niagara Falls, N. Y.
John M. Shrigley, Williamson School, Pa.
M. J. Smith, Philadelphia.
Walter F. Smith, Philadelphia.
Chas. Stein, Philadelphia.
O. R. Sweeney, Philadelphia.
E T. Takamine, New York City.
H. S. Taylor, Princeton, N. J.
Philip Uhl, Philadelphia.
Mrs. L. D. Vorce, Detroit, Mich.
L. M. Willey, Schenectady, N. Y.
Mrs. L. M. Willey, Schenectady, N. Y.
Mrs. J. A. Yunck, S. Orange, N. J.

MEMBERS ELECTED AND QUALIFIED

Since Last Membership List (Dec. 31, 1914).

January 1:	Keller, Oran	New Brunswick, N. J.
" 1:	Smith, Walter C.	Chrome, N. J.
" 12:	Burman, B. F.	Carnegie, Pa.
" 12:	Butts, Allison	Chrome, N. J.
" 12:	Tower, O. F.	Cleveland, Ohio
" 13:	Mulligan, J. J.	Perth Amboy, N. J.
" 14:	Grymes, E. S.	New Brunswick, N. J.
" 18:	Maier, C. G.	Niagara Falls, N. Y.
" 19:	DeForrest, C. M.	Tonawanda, N. Y.
February 1:	Schlatter, H. C.	Niagara Falls, N. Y.
" 4:	Thum, Wm.	Hammond, Ind.

February 4:	Gaby, F. A.	Toronto, Canada
" 5:	Somdal, J. A.	Massena, N. Y.
" 12:	Bonnevie, H.	Rjukan, Norway
" 18:	Murphy, R. K.	Sydney, Australia
" 18:	Forbes, S. G. S.	Cambridge, Mass.
" 18:	Baker, R. E.	Madison, Wis.
" 25:	Rippel, E. G.	Buffalo, N. Y.
March 8:	Bovee, B. A.	Milwaukee, Wis.
" 9:	Bear, S. L.	Pittsburgh, Pa.
" 9:	Teeple, O. J., Jr.	Haskell, N. J.
" 12:	Seguine, Wm., Jr.	Cleveland, Ohio
" 16:	Frick, F. T.	Anaconda, Mont
April 1:	Chapin, H. C.	Cleveland, Ohio
" 1:	Hoffmann, J.,	Newark, N. J.
" 5:	Curtiss, J. L.	Buffalo, N. Y.
" 8:	Needham, H. H.	East Orange, N. J.
" 8:	Strauss, F. A.	Wilkes-Barre, Pa.
" 8:	Boynton, W. H.	Grasselli, N. J.
" 15:	Ruel, A. J.	Sandpoint, Idaho
May 1:	Henderson, E. G.	Windsor, Ontario, Canada
" 1:	Johnson, J. E., Jr.	New York City
" 1:	Kleinfeldt, H. J.	Newark, N. J.
" 4:	McKnight, W. A.	Niagara Falls, N. Y.
" 4:	Landau, A.	Toronto, Canada
" 4:	Hibbert, H.	Pittsburgh, Pa.
" 4:	Stevenson, R.	New York City
" 4:	Wills, W. H., Jr.	South Bethlehem, Pa.
" 5:	Winter, E. J.	Niagara Falls, N. Y.
" 5:	Harvey, F. A.	Syracuse, N. Y.
" 7:	Moerk, F. N.	Oak Lane, Philadelphia, Pa.
" 11:	Igarashi, T.	Schenectady, N. Y.
" 31:	Mays, S. N.	Niagara Falls, Canada
" 31:	Goldstein, P.	London, England
June 8:	Hamann, A. M.	Niagara Falls, N. Y.
" 8:	Boice, E. N.	Newark, N. J.
" 8:	Reed, S. A.	New York City
" 8:	Foster, R. D.	Newark, N. J.
" 8:	Kutz, M.	Philadelphia
" 14:	Newman, P. J.	Manhattan, Kansas
" 14:	Yount, A. G.	Pittsburgh, Pa.
" 14:	Swartley, H. R., Jr.	Marion, Jersey City, N. J.
July 16:	Taylor, H. S.	Princeton, N. J.
" 16:	Cox, S. F.	Princeton, N. J.
" 19:	Ralston, O. C.	Salt Lake City, Utah
" 19:	Curfman, F. G.	St. Louis, Mo.
" 19:	Czarnecki, F. C.	San Francisco, Cal.

The Presidential Address, delivered at the Twenty-seventh General Meeting of the American Electrochemical Society, at Atlantic City, N. J., April 22, 1915. President-elect L. Addicks in the Chair.

THE AMERICAN ELECTROCHEMICAL SOCIETY IN ITS EXTERNAL RELATIONS

By F. A. Lidbury.

Eight years ago, when the American Electrochemical Society was last the subject of a presidential address,[1] the Society was faced by many serious problems relating to its growth and the continuance of its existence. Finance, the provision of papers, the attendance at meetings, questions regarding publications, matters involving even its independence were the subject of anxious thought and discussion. The successful growth, both extensive and intensive, of the society since that time must be a matter of extreme gratification to those whose devotion, energy and wisdom at an anxious period of its existence guided the Society in the direction which has led to its subsequent well-balanced development.

There comes a stage in the development of every organization such as ours at which the cultivation of the primary objects of its existence no longer demands all its efforts; it becomes free to devote itself to external activities, and to represent its membership and what it stands for in the larger affairs of life. Of course, it need not do so. A voter need not exercise his franchise; but we do not call him a good citizen for the omission. An innocuous reputation for respectability and learning can easily be maintained by any scientific body which carefully avoids contact with objectionable external realities; but it is the kind of reputation which attaches to that paragon of respectability who "passed by on the other side." In the last few years this Society has shown gratifying indications that it takes no such narrow view of its duties or its interests; and I hope and expect that its activities in external matters will be progressively intensified and broadened.

[1] Carl Hering, Trans. Amer. Electrochem. Soc., **11**, 17 (1907).

Perhaps as good an illustration as any of the direction in which our duties and our interests lie can be found by considering our relations to current tendencies in government. The extension of legislative and bureaucratic activities which the last few years have seen has been too widely regarded by intelligent persons as a manifestation which would play itself out, on the principle that "if the fool would persist in his folly, he would become wise." Not only has this optimistic expectation not borne fruit, but reliance on it has to a large extent prevented the offer of information and guidance from those in a position to give it. There are signs that men of business are realizing their mistake in the matter, and it is time that the man of science and the engineer also realized theirs. What cannot be averted can at least be guided into intelligent channels.

The engineer—take the word in its widest sense—has been worrying about these matters for a long time; and occasionally he comes to the conclusion that what is needed is representation of himself in legislative bodies.[2] He had better remember that legislation is really lawyers' business. If the scientific and engineering professions would worry less about their "status" and pay more attention to making their opinions heard and their recommendations respected, they would cease to be bothered about the undue proportion of lawyers in legislative bodies. For, on the whole, these lawyer-legislators are not so scornful of information and advice as we are inclined to believe. They try to get both whenever they can, and, when the practical business man, the technical man, the engineer held aloof, they went to the university professor and, when he was not available, to the charlatan and the agitator. They have shown their power of discrimination by preferring the professor; they instinctively felt that he knew more. If his guidance has led them into difficulties, it is because his truths are too often colored by his theoretical idiosyncrasies, and not founded on a pragmatic basis. Until we have given the legislator all the assistance in our power, we are obviously not in any position to accuse him of spurning it. Nor does it particularly matter if he does; for the power of an intelligent minority, however small, is tremendous, and there is

[2] See, for instance, E. W. Rice, Jr., on the "Status of the Engineer," Proc. A. I. E. E., 34, 648 (1915).

no man more sensitive to well-informed criticism of sufficient publicity than your legislator, unless it be your bureaucrat.

I have attempted to indicate the extent to which the intelligence of government of a democracy is dependent upon the co-operation of its intelligent elements, and the extent of the responsibility in this regard of those professions which claim to embody the application of intelligence to industrial operations. A little self-examination will show that a well-defined portion of this responsibility rests upon the American Electrochemical Society. We need have no false modesty about it, either in regard to what we represent or to what we are. We represent a branch of the chemical industry whose products are of such importance to the general industries of the country that, in spite of its youth, its absence at the present time from among the industries of the country would cause such industrial disturbance that the plaint of the wearer of many colors, always imminent but not up to the present moment audible, would pass unnoticed. As a society, we are unusually representative. We embrace in the personality of our members and in the scope of our discussions the practical as well as the theoretical, the commercial as well as the technical; as a consequence our organisation is capable of considering all phases of any question which comes within its scope. We have had a healthy growth, and our functions are normal; we do not suffer from overgrowth or uncorrelated parts, nor are we weakened by the overdevelopment of any particular activity. We have a representative constitution and its consequence, a responsible and responsive management. Finally, we are entirely independent, not only of outside influences, but also of any one class of internal opinion; the diverse nature of our membership guarantees us against the dangers of a narrow point of view. Our duties are proportional to our responsibilities. It will not be necessary for us to look around for subjects to which to devote our attention; many of these are clear; on some we have already made a beginning, some, still more important, we have not had the temerity to touch.

Perhaps there is no subject which will better illustrate our sins of omission (in common, I hasten to add, with many technical bodies equally interested in the matter) than our inaction

in regard to legislation concerning water-power. This is not the occasion on which to discuss the limitations which have been imposed upon the development of power at Niagara Falls; nor, if it were, should I be able to add anything to the treatment of the subject by my predecessor in his presidential address at the last New York meeting.[3] I wish not to touch upon the controversial aspects of that question, but to point out that we have allowed the whole matter to go by default. A combination of fortunate circumstances enabled our industry to grow in the last twenty years to the point where we are somewhat more than independent of foreign manufactures in electrochemical lines. What we do not suffer from we do not realise, and while almost everyone who reads the newspapers is able to growl at the comparatively small development of the organic chemical industry in this country, an appreciation of what the same condition in the electrochemical industries would mean is probably not general even among our own members. It was not alone the reliability of Niagara power or its comparative cheapness which made it a vital factor in the development of our industries; it was the combination of these with a favorable commercial location. It is quite possible that had the development of power at Niagara Falls been prohibited from the beginning instead of throttled in its infancy the growth of electrochemical industries in this country might have so fallen behind that in other lands as to make us as dependent in this respect as, for instance, we are for dyes. We owe it to ourselves, both individually and as a society, to take every opportunity of bringing about a wide-spread knowledge of this situation. The electrochemical industry is already paying the penalty in the way of increasing scarcity of power and rising prices in the Niagara district, for allowing matters to take their own course. Turning to the broader aspects of power development, we find that curious ideas have received governmental sanction, and even action, without any attempt at correction by us. For instance, that water-powers could be best developed by preventing people from developing them—we actually approved of this idea in a solemn resolution[4]; that conservation

[3] E. F. Roeber, Trans. Amer. Electrochem. Soc., **25**, 17 (1914).
[4] Trans. Amer. Electrochem. Soc., **16**, 3 (1909).

and the interests of the people and particularly efficiency would be best subserved by preferably connecting water-power plants to the loads of precisely the lowest load factors known.[5] If ideas of this description are acted on through lack of careful and intelligent controversion, who is to blame for the result—the ignorant, or those who know and keep silent?

I turn to patent legislation. Here we have, chiefly through the tireless energy of one of our past presidents, a record of some activity. But much more ought to be done. The combined efforts of many societies such as ours have succeeded in averting some very serious consequences of ignorance; but the whole question calls for a great deal of constructive effort. I know of no matter which presents to us so many difficult aspects; and not the least difficult is the danger that in trying to do justice to the "inventor" we may fall into the error (so common among inventors themselves) of regarding him as "the whole thing." So many of us have to take a matter where the inventor leaves off and make it work that we know better; we have a peculiar knowledge of this subject, and it is our duty to see that it is not overlooked.

We are governed more and more by commissions, officers, and bureaus. In so far as the operations of these agencies are of a restrictive nature, untoward results, where they occur, are usually due to ignorance being left to its own resources. A watchful readiness to extend co-operation, advice, information, and assistance in matters which come within our scope will help to correct this. It is likely, however, that we shall come more frequently in contact with agencies of a constructive nature, of which the scientific bureaus of the government may be taken as typical. These do a great work, and our respect and admiration for it is likely to be proportional to our knowledge of it. Their primary purpose coincides with our own, the assistance of the application of knowledge to industry. To a great extent their usefulness will depend upon us and our *confreres* in related lines, upon the use we make of them, upon the fertility of the suggestions they receive, upon the extent of the support of their efforts. It is so easy to take beneficial activities for granted that it is necessary continually to remind ourselves that a given

[5] Cf. Met. & Chem. Eng., **11**, 117 (1913).

amount of energy devoted to the support of existing valuable agencies will produce many times the results which would follow its application in other directions. The cultivation of many fields of investigation which would otherwise lie dormant because, being everybody's business, they are nobody's business constitutes a peculiarly useful branch of governmental activity and we ought by suggestion and support to lend every possible assistance to those to whom it is entrusted. The development of such relations with them would result in a duty of another description falling upon us as representing the people in these matters; in so far as such governmental activities touch upon our sphere, we should impose a measure of accountability. We should assist in checking expenditures on unnecessary work, or on duplication; we should insist, in view of the conception of bureaucratic infallibility held by the uninformed, on accuracy of statement in government publications, and of the elimination from them of collections of untrustworthy or incorrect information. We should carefully examine the recent tendency to regulate certain branches of industry nearly related to ours by instruction, by suggestion, even by the development of industrial processes. Some aspects of this tendency are open to serious objections on principle; but it is evidently with us for trial at least, and we must do what is possible to encourage its useful, to discourage its harmful aspects. We should insist upon a careful verification of all statements of the commercial aspects of governmental work of this description as well as of its technical features. It is impossible to believe that governmental agencies such as I have alluded to could fail to gain in value by the inculcation of a sense of responsibility to the technical societies of the country. It would probably reduce the temptation to play to the gallery; it would at any rate prevent the deplorable spectacle of a member of the cabinet announcing a technical discovery originating in his department in terms of combined ignorance and extravagance of claim which would almost justify exclusion from the mails if employed by an ordinary company promoter.

Multiplication of instances in quite other fields of action would be easy. I have taken quasi-political cases because they afford

perhaps the clearest illustrations for the purpose of exposition. I must turn, however, to the considerations of means, of the "adjustment of internal to external relations." The stimulus must come largely from the individual, the unofficial member. He must be ready to bring up subjects of general interest; the officers and the Board must be equally ready to afford facilities for their general discussion and their thorough consideration by active and competent committees. However intense and unanimous the feeling of the membership may be upon any particular matter, the effectiveness of its expression will necessarily depend in the last resort upon the energy and ability of some committee. There is an abundance of suitable committee material in this society; and there will be no difficulty in getting matters in which you are sufficiently interested properly handled. The discussion of external matters at our meetings would also tend to stimulate the exercise of the power of individual members for educating the uninformed.

Co-operation with other societies should be not only willingly given, but sought after. In general, co-operation with other societies forms an important part of our external activities. Even the little which has been done has been productive of results. A single joint meeting, for instance, with the American Electroplaters' Society some years ago has not only led to a considerable increase in interest in electroplating work in our own society, but has given the impetus to some very interesting and promising developments in electroplating circles in more than one locality. But the most interesting steps in inter-society co-operation have been taken for us by our flourishing New York Section during the last few years. We are indebted to that Section and to its capable chairmen for showing us to what extent many dominant subjects need joint sessions for their proper presentation and discussion; and that brings me to the suggestion that the encouragement of local sections is the readiest means of fostering a healthy internal and external development. By their very nature they are able to maintain a much more continuous chain of interest; they come more readily in contact with the problem of the moment, the external problem; they touch it with less hesitation, less formality.

I cannot conclude without expressing my admiration of the excellent example which Dr. Roeber has set us in the editorial pages of his Journal; pages which have often so thoroughly represented the society in external affairs that we may very well be pardoned, though not excused, for having felt any exertions on our part possibly superfluous.

A lecture delivered by invitation at the Twenty-seventh General Meeting of the American Electrochemical Society, in Philadelphia, at a Joint Session with the American Electroplaters' Society, April 24, 1915; President F. A. Lidbury in the Chair.

THE DEVELOPMENT OF ELECTRO-ANALYSIS IN AMERICA.

By Edgar F. Smith.*

This is the fourth time in the history of this Society that it has met at this University. Its first meeting, after its organization in this city in 1902, was held here. We feel highly honored by your visits, and I think it is a very proper thing that since the organization was instituted here it should call upon us frequently. Where else in the United States would it find an atmosphere so congenial as the University of Pennsylvania? (Applause.)

Recall, please, that it was in 1835 that Robert Hare, then Professor of Chemistry in this University, dissatisfied with what he read in a Bakerian lecture delivered by Davy upon calcium, set about to find a method that would give him that particular metal in better form than it had been obtained by Davy. You recall that before Davy's experiments lime had been placed upon a plate of platinum, which served as an anode. A crater was made in the upper portion of the lime into which mercury was poured, and an iron wire suspended in the mercury was connected with the cathode of the battery. It was that mercury which, according to Davy, received the calcium, and the resulting amalgam upon distillation left the calcium in the form of a silver thread. Dr. Hare was dissatisfied with the experiment of Sir Humphry Davy, and it occurred to him that perhaps he might electrolyze the aqueous solution of some calcium salt, using mercury as a cathode. This he did, driving the calcium from the solution of its chloride into the mercury. The resulting amalgam he distilled. This is the first record of the use of mercury as a cathode in the electrolysis of aqueous solutions.

I like to think of Hare as having brought to our attention the

* Provost of the University of Pennsylvania.

use of mercury as a cathode. You all know to what extent you who make caustic soda use it as your cathode.

Again, in 1880, Wolcott Gibbs undertook further experiments, probably because he was here in 1844 working with Robert Hare, and in his conversations with him heard something about the use of mercury as a cathode. 1844 would only be nine years after 1835, and it is not at all improbable that Hare talked to Gibbs about what he had done in getting calcium; so in 1880 we find Dr. Wolcott Gibbs suggesting in electro-analysis this process: using a beaker, pouring mercury into it, and then, by means of a wire, allowing the mercury to be made a cathode. He introduced the solution of a metallic salt and suspending a platinum wire in the liquid passed the current, and the metal was precipitated into the mercury cathode. This Dr. Gibbs did in 1880, and again in 1884.

Nobody paid any attention to him. Nothing was heard of the use of mercury as a cathode for years afterwards. Dr. Gibbs told in his paper how he was able to deposit copper in the mercury, and that the solution above the mercury contained no copper. He also electrolyzed a solution of nickel sulphate in the same manner, driving the nickel into the mercury, but did not concern himself with the determination. He took for granted, that because the solutions of copper and nickel had become colorless, they had lost their metal. In 1884 he learned that it would be possible by weighing the beaker and mercury before and after the experiment, to get the copper, we will say, and by removing the liquid from the beaker, the anion—the other component of copper sulphate—the sulphuric acid might be obtained by titration, but he never did any work on that, and never published anything about it.

Some years ago we were attracted to this suggestion of Dr. Gibbs, and those of you who have followed electrolysis know that we used it quite extensively. We then began to determine metals in this laboratory, using mercury as a cathode. And now, you see why I said a while ago that I think the Electrochemical Society ought to feel at home in the atmosphere of this University.

We have done little more than determine and separate the metals with the help of the current. We have isolated a few.

We isolated calcium here in 1903, and obtained greater quantities than had been obtained before. I sent a piece of calcium to Dr. Gibbs, and received reply that he had never expected to look upon so large a piece of the metal that his teacher Robert Hare had obtained in threads. It was surprising to the good Doctor. I might say, also, that it surprised us that we were able to get it.

I do not think that we have contributed anything to electro-chemistry outside of this analytical work, but it is very interesting to me, and if you will pardon me for a moment, I will recall my own experience in this particular field. Here sits Dr. Hering, an honored Past-President of this Society. Years ago as a student under me, in the old laboratory in College Hall, I taught him his qualitative analysis and some other things, and at that time I had charge, not only of the students in qualitative analysis, but of the students in quantitative analysis. One of the problems we frequently gave the students in quantitative analysis was the determination of copper in copper sulphate. Those who have analyzed this salt know the methods given by Fresenius and in other text-books. When you think of precipitating copper from a boiling solution of sulphate, with a slight excess of caustic potash, and recall how you tried to get rid of the alkali, and recall how when, finally you had the oxide of copper, and you saw the crucible in the balance growing heavier every moment—when you recall these experiences, then you can understand how, as a young teacher, I felt in facing these boys placed in my charge, when I tried to make excuses for the shortcomings of the method.

I was willing to welcome a method for the determination of copper that would be more exact, more satisfactory, than any we had, and so looking back I found a statement of the determination of copper in 1865, by Wolcott Gibbs, with the help of the current, in other words, the electrolytic determination of copper, and we put the process into action up there in the old laboratory. I had never used the method either as a student or as an instructor. I then began to have the boys determine copper with the help of the electric current. Was there anything being done in 1878 in this country for electro-chemistry? Recall, there was not a single thing being done in electro-chemistry, with the

exception of electro-plating. We scarcely called that electro-chemistry; we designated it as electro-plating. Nothing was being done at that time in electro-chemistry.

Then there was this other problem that every student that has worked in quantitative analysis has had: the separation of copper from cadmium. You know the old method: add an excess of ammonia, the solution is blue, decolorize with potassium cyanide, and then pass hydrogen sulphide to precipitate the cadmium. That was a reasonably good method, in its way, but the electric current helped us out very materially. On turning to the books I could not find that there was a single sentence relating to the action of the current upon cadmium salts, so that we had to try various methods to ascertain what the current would do with them. We weighed out a quantity of oxide of cadmium, dissolved it in acetic acid, added water and placed it in a crucible of 50 cubic centimeters capacity. That crucible was set in a ring of heavy copper wire, connected up to an electric current. The latter was allowed to run, and to our amazement we found cadmium precipitated on the inside of the crucible. I found on raising the level of the liquid that there was no more metal precipitated out on the fresh platinum surface. I recall with what joy I reweighed the crucible, and found that the weight of the cadmium corresponded to the amount of metal in the oxide I had used. I went to Dr. Frederick A. Genth, and holding the crucible before him, asked, "Doctor, what is that?" He had a rotund figure which prevented him from coming up to the table, and as he looked at me he shook his head. He did not know. He simply waved it aside. I went back and repeated the experiment five or six times, each time carrying to the Doctor the deposit of cadmium on the platinum dish, but was waved off. I said—"This is cadmium, Doctor, and it is quantitatively precipitated." "Oh, oh," that's all the encouragement I received. So I went on and kept in mind the point that the current helps to separate cadmium from copper. Definite amounts of copper oxide and cadmium oxide were brought into solution in my old crucible, and to that solution of the two salts was added a definite volume of nitric acid of a certain specific gravity. We used to say in those days "two or three drops," but thank fortune we

have since then been obliged to determine how much a drop is. At that time we forgot to say anything about the specific gravity. Nowadays we have to indicate the specific gravity. We forgot in those days to say exactly what amount of solution we had in the crucible; we would say it was somewhere about 50 cubic centimeters, but nowadays we have to be exact.

We exposed the mixture of the two metals, in the presence of a certain amount of free nitric acid, to the action of the same old current. Dr. Gibbs said he precipitated copper with the help of a "brisk" current. We did not undertake to determine the strength of the current. We knew nothing about that side and were not interested in it. The question was: Will the current throw out one of these metals and leave the other? When I could show the separation to Dr. Genth, and he gave me no sign at all, not even a grunt, I was disappointed. When I showed him the cadmium and he indicated in no way satisfaction or pleasure, or any other emotion, it was a little bit disheartening. But the lack of advice from Dr. Genth acted as a spur for me to try something else.

When I began to study electro-analysis no one else in the country was working on it or upon anything pertaining to the electric current. I am a kind of Father of Israel, when you consider electro-chemistry, although what I have done is not what you may care a great deal for. Being a chemist, pure and simple, I am looking at the side that chemistry, pure and simple, would take into consideration. I have often said: You can put your batteries and dynamos outside of the walls of the building, all you need do is to run in a cable and give me the current. Some say there are no chemists: Mr. Addicks says the chemists are all gone. But here, if you please, is one. (Applause.)

I wanted to convince that brainy old German chemist, Dr. Genth, that the electric current could do something in analysis, which was his pet field. He was working in the next room on a mineral called gummite, which is rich in uranium, and also contains sodium. He was telling me of the difficulty that one has to separate uranium from sodium. Those of you who have tried it will endorse all he said at that time, but no matter whether you have tried it or not, you would endorse it if you

heard him say so. I could not help but ask myself: What is this gummite? I looked up the mineralogy and found out about it. I found if the mineral is taken up, and you get rid of the silica, the other constituents might be had in aqueous solution. I could find nothing about the action of the current on uranium salts.

I concluded, in view of the previous success we had had, that I would make an acetate electrolyte. I found potassium and uranium acetate, one of the most beautiful salts we have in chemistry, quite soluble in water. Had the Doctor known I was going to take any of that precious material he would have locked it up, but I got a bottle anyway. I took it to my room and weighed out the quantity of the crystallized salt. I happened to say, casually: "Doctor, is the acetate of uranium and potassium that you made some years ago, that you have around here, really pure?"

"Yes," he replied, "that is chemically pure, I made it myself. That is all right. I do not know where that bottle is. It is around somewhere. I must look it up, I do not like to let it stand about, some one might come in and use it. You might use it for uranium tests."

"It's pure, though?"

"Yes, it's pure."

"That is what I wanted to know." I weighed off a portion of the double acetate of uranium and potassium, dissolved it in water, put the solution in a crucible of 50 cubic centimeters capacity, and let the current go. In a few minutes I found it plating out on the platinum cathode a yellow coating, the liquid losing its yellow color. Then I noticed a coating which was varying, with black spots. I suppose I had precipitated the hydrated oxide, but when it was black I thought I was getting the metallic uranium, as the deposit was upon the cathode. After a while the entire deposit became black in color. After carefully introducing water to raise the level of the liquid, I turned on more current, but nothing came out on that exposed platinum surface, so I quickly disconnected the crucible and rinsed it out, poured out the colorless liquid and washed the deposit with water. I did not know what it was. I saw it was not metal,

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although it was black, and showed luster. I ignited it, and knew it would go to the 3 : 4 oxide.

I made my calculations for uranium, and found it to be within 0.2 milligram of the amount present in the double acetate of uranium and potassium. I worked all night on one occasion and repeated the experiment to satisfy myself that I had a new quantitative method for the determination of uranium, and further a separation from potassium. Of course it would also be a separation from sodium. I went to dear old Doctor Genth and showed him the deposits. He made no comment, but said, "I have this problem," and then he stated the problem of separating uranium from sodium, and asked if I would make that separation if he provided the acetate solution. I said, "Certainly." So he gave me an acetate solution saying: "This contains nothing but uranium and sodium." I placed the solution in my crucible and after the electrolysis made my report. The next day he asked me to try another separation. I made five experiments, but never knew whether any one of the five was correct or not, but ten days after I had begun to do the work for him he called me to his private office and showed me his note book containing his own results. I noticed that my results in the separation of uranium and sodium were identical with his. He remarked: "Your method must be a very good method."

From that time on to his death Dr. Genth was a convert to electro-analysis, and from that time I think I was a convert. I felt that there was not anything under the sun which we could not determine with the help of the current.

For industrial purposes, what we had in mind was the determination of metals by the help of the electric current. We gradually learned something about current strength, about voltage, we had respect for the distance of the electrodes from each other, and for the temperature; in other words, we learned respect for those things which you electrical engineers respect. We have also learned something about amperes. We continued until electro-analysis became a real addition to analytical chemistry. I am sure that all who use electrolytic methods prefer them to the old gravimetric methods. The current does the work.

I could talk at great length on this subject, but my object was

merely to show you how I came into the field of electro-analysis, which is but a corner of the great field in which you are interested, and which you are cultivating. We have stayed in our corner.

As it took years to accomplish some of these methods, so it would take hours and days to tell the whole story.

Now, we have one or two things to show you. Dr. Lukens has been traveling through the field of electro-analysis with me. He wants to exhibit a means of agitating the electrolyte. He employs the device of running hydrogen through the solution while it is being electrolyzed; that is all. You will find after a few minutes of agitation that the metallic copper has been thrown out completely. It is a thing, fortunately, which introduces no expense in the laboratory.

I do not know how many of you have determined cobalt quantitatively. I want you to look at this [exhibiting specimen]. Do you think that is cobalt? It does not look like the metal. You can examine it more closely afterwards. We spent a good deal of time in trying to determine cobalt with the help of the current. We do not care for the old gravimetric methods and volumetric method. We have had enough experience with them, and we are only too glad to have the current determine it for us, and it does determine it for us, but here is something new. This is the dioxide of cobalt which has been precipitated on the inside of this platinum dish. All of the cobalt is in that form. In the electrolysis of cobalt solutions we sometimes find a little peroxide of cobalt on the anode, just a little, and we have various devices to get rid of it. But here you see all of it, all of the cobalt that was in the solution in this dish originally, is left on the dish, which is the anode. It is there as hydrated dioxide. You may ask me how we get it. Let a current of about 2 volts and 0.8 ampere act on the double fluoride of cobalt and ammonia. If you use as an electrolyte ammonium cobalt fluoride, no cobalt goes to the cathode under 8 volts. Two volts is sufficient to precipitate it completely on the anode, with a current of 0.8 ampere. We have a number of determinations here which will satisfy any one that it is an excellent method, so far as this particular metal is concerned. We can convert it into 3 : 4 oxide and weigh it

as such, multiplying the quantity by a factor which will give us the metal in the oxide.

What bothers you when you talk about cobalt? You think of nickel. You think of the separation of nickel and cobalt by the double nitrite method with potassium, etc. You know there is not an electrolytic method for the separation of nickel and cobalt. The current which precipitates this cobalt will not precipitate any nickel when it exists as nickel ammonium fluoride. Doctor Lukens has a separation here showing results in which he gets within a tenth of a milligram of the proper amount of cobalt, in the presence of nickel.

The test which is regarded as the most complete for the detection of nickel is dimethyl glyoxine. It gives a precipitate with nickel. It does not do more than brown the color of the cobalt solution. It is an extremely delicate test, and with that reagent Dr. Lukens has not been able to find any nickel in the precipitated cobalt. Hence we think we have a method for the separation of cobalt and nickel which may be carried out in a most satisfactory way. The nickel goes to the other electrode. If we should happen to use a strong enough current, we can precipitate them simultaneously, the nickel as metal on the cathode, and the cobalt on the anode as dioxide.

This is the only new thing which I have to show you in electro-analysis. If you will read the literature, you will find there has not been very much done within the past three years. It has been a period devoted more to the perfecting of the methods which have already been found. I do not know those of you who are interested in cobalt; it may be that there are not any here who are interested in it. We feel perfectly confident in the new method for the determination of the metal. We must find something which will give us the assurance that there is not any nickel in cobalt—a test that will be more reliable than that with dimethyl glyoxine. I wish we could get it. Think of the years many men interested in this work have been trying to get a real good method for the separation of these two metals. We may go to the fourth group and separate manganese from zinc, and cobalt from manganese, and cobalt from zinc, but no one raises the question: Can you separate nickel from cobalt by elec-

trolysis? We study the subject further, make two or three successes, try out this or that thought expecting to get good results, and hope to, but the exhibit before you is the nearest we have come to a realization of our ideal.

DISCUSSION.

S. D. BENOLIEL: I would like to know whether in the separation of cobalt and nickel the best method is to separate the cobalt first and the nickel afterwards, or whether it is better to effect the separation simultaneously, depositing nickel on the cathode and cobalt on the anode? Which method is preferable?

H. S. LUKENS: So far as I have discovered, it is better to separate the cobalt first. Much to our disappointment we found the agitation of the electrolyte by any means that we might employ seemed to offer no advantages in this separation. As a matter of fact, in the case of cobalt, by rotating the electrolyte the cobalt oxide is precipitated in a non-adhering and granular form, whereas the precipitate made in the electrolyte that is alluded to is quite adherent, as you see. It can be washed out, even, by projecting a stream of water directly against it when it is first precipitated. It is precipitated probably as hydrated peroxide, which on ignition passes over into Mn_3O_4.

When I first attempted to separate nickel and cobalt, I found some nickel was deposited with the cobalt, even with an electromotive force as low as 2 volts. The current for such a small electromotive force was very low, and it took considerable time to deposit any quantity of cobalt. To eliminate this disadvantage I platinized the cathode, and thereby cut out the over-voltage due to hydrogen, increasing the current, so that I was able with 4 gr. ammonium fluoride to get about 0.8 ampere through that solution with a pressure of two volts. Much to my surprise apparently no nickel was deposited on the cobalt under these conditions. I am not quite sure, because there has been a slight overweight noticed in the cobalt, indicating that some nickel is present in the cobalt deposited.

PRESIDENT LIDBURY: How about the presence of other acids, to what extent is their presence to be guarded against?

H. S. LUKENS: I can only say this: the work started with the idea of investigating fluorides as electrolytes generally; we had gotten as far as nickel and cobalt when we were attracted by the difference in behavior. Having nickel and cobalt together as fluorides seems to work no better than if we started with nickel and cobalt as nitrates and added to them a solution of ammonium fluoride. The presence of hydrochloric acid is a decided disadvantage and prevents the formation of the cobalt oxide, and nitric acid has proven to be the only acid which effectually tends to prevent the cathode deposition of cobalt. Hydrochloric acid and hydrofluoric acid have both been used, but they interfere with the deposition of the cobalt.

S. D. BENOLIEL: Has nitric acid any effect in helping the oxidation of cobalt?

H. S. LUKENS: It apparently does not influence the deposition of the cobalt in any way, but does prevent the formation of cathode deposits.

PRESIDENT LIDBURY: How would you apply the method in ordinary analysis, when, for instance, you get the nickel and cobalt separated as sulphides, what would the further procedure be?

H. S. LUKENS: Dissolve these sulphides in nitric acid, evaporate to dryness on the water bath, remove the excess of nitric acid, take up with water, add ammonium fluoride and nitric acid as an electrolyte.

PRESIDENT LIDBURY: Do you get sulphuric acid in the solution?

H. S. LUKENS: Very little sulphuric acid under these conditions.

PRESIDENT LIDBURY: That would not interfere?

H. S. LUKENS: Not in that quantity.

PRESIDENT LIDBURY: Can you redissolve the deposit and then electrolyze again and remove the nickel?

H. S. LUKENS: I have not tried that. My own time is limited, and the actual work of separation has been confined within the last three weeks, and we have not been able to try everything we would like to try. This represents the progress we have made to date. I will say for Dr. Frary's information that the cobalt was precipitated as dimethyl glyoxine, and the nitrate prepared from that. The cobalt was prepared as cobalt purpureo chloride, with subsequent transposition into nitrate.

FRANCIS C. FRARY: Have you tried adding a little, a gram or less, of nickel to the solution of your cobalt precipitate to see if you can get a reaction with the dimethyl glyoxine?

H. S. LUKENS: Yes, I did, and you can get a reaction. Just the quantity of nickel necessary to add I can not say exactly.

JOS. W. RICHARDS: There is a similar phenomenon when you are depositing lead peroxide on the anode; it takes about six percent of free nitric acid in the solution to prevent lead depositing on the cathode; otherwise you get lead on the cathode as well as lead dioxide on the anode. Many practical hints and suggestions have come to practical electro-metallurgy from electro-analytic methods and I believe our friends in Canada would be interested in knowing of this comparatively simple electrolytic separation of nickel from cobalt.

This may indeed lead to a practical method of separating the two metals.

A Discussion at a Joint Meeting of the New York Sections of the American American Institute of Mining Engineers and the American Electrochemical Society, January 6, and called up for further discussion at the Twenty-seventh General Meeting of the American Electrochemical Society, at Atlantic City, N. J., April 23, 1915.

SOME PROBLEMS IN COPPER LEACHING.

L. D. Ricketts, New York, N. Y.—In recent years the metallurgical field of the copper industry has expanded greatly, the copper ores have become lean and diverse in character, and we are obliged to treat such ores on a very large scale.

On the commercial side, the operating and consulting staffs of the great mining companies have been enlarged and organized, and no great capital expenditure is decided upon until it has been investigated and recommended by a highly organized force of specialists as a committee.

I believe that in the scientific field and in the most valuable procedings of our various societies the old idea of one-man point of view and one-man treatment of principle and detail together has been splendidly developed and should continue, but for the advancement of our art we should deliberately discuss subjects among ourselves in order to do away with the idiosyncrasies of the individual and to gain a composite view representing the best thought of many men.

In the development of new ideas leading to the introduction of new methods, the societies could enlarge their present great field of usefulness if such discussion be had, and in my opinion further great good could be done if a number of men of different qualifications and experience would join in preparing a joint book, each dealing with his particular problem, but consulting the other men. In this way individualism would be preserved and various processes would be described, and if properly reviewed the paper would be palpably capable of analysis, and the student would have at his command the associated efforts of a group of qualified engineers.

I have neither the time nor the qualifications to make an investigation and study in detail of hydro-metallurgical processes, but for some years I have foreseen the development of such

processes, and I have a deep interest in the subject and have given it in some of its phases careful consideration from a long-distance viewpoint. I have assisted in directing many experiments and in reviewing the merits of many processes, and am glad to make some introductory remarks with the understanding that other gentlemen present will freely and candidly enter into the discussion and help to fill out the few bare bones that I can uncover. You will see in my remarks that I am controlled very largely by operating demands. No matter how beautiful the process, simplicity and cheapness of operating costs are the main features that appeal to me, and complexity and increased costs only appeal to me if they definitely promise an increased yield that will more than offset the increased expense; for, given the grade, the maximum profit per ton is demanded.

As you all know, there has been a very large development of deposits of lean copper ores in the Southwest in recent years, and this region has rapidly developed until in the aggregate it produces more copper than any like area in the world, and it still has a large increase of output ahead of it. The vast mass of these lean deposits consists of sulphide ore, and until recently these sulphides alone have attracted serious attention. It is well known, however, that there are large tonnages of oxidized copper ore associated with the lean porphyries.

A few years ago the Calumet & Arizona Mining Co., upon the recommendation of J. C. Greenway, took an option upon a majority of the stock of the New Cornelia Copper Co., whose mining properties are at Ajo, in southwestern Arizona. Mr. Greenway directed systematic drilling upon this property, followed by the sinking of some 70 shallow shafts for test purposes and the sinking of two deeper shafts, with considerable underground development, for the purpose of testing and checking the grade of the sulphide ore. The stock was purchased.

The matrix of the ore is an eruptive granite. There is no overburden. The chalcocite has been oxidized nearly as fast as formed. The zone of transition from oxidized minerals to primary sulphides is narrow. The oxide and sulphide ore is remarkably uniform in grade. Ira B. Joralemon's paper, in the *Transactions*,[1] describes this deposit. He shows that there are

[1] Bull. Am. Inst. Min. Eng., No. 92, August, 1914, pp. 2011 to 2028.

about 40,000,000 tons of ore containing 1½ percent copper, and the tonnage is divided into about 12,000,000 tons of 1½ percent oxidized ore and 24,000,000 tons of sulphide ore, with about 4,000,000 tons of mixed oxide and sulphide between. If the grade be dropped to an average of less than 1½ percent, these tonnages would rapidly increase.

In parallel with this development, oxidized ore in notable tonnages has been found in the Globe mining district. This ore is more scattered, and, on the whole, is leaner than the Ajo ore, and frequently has a large capping of overburden. In the aggregate, the Inspiration Consolidated Copper Co. alone now has over 15,000,000 tons of oxidized ore running about 1.3 percent, and a probable tonnage in addition. There are other mines in other districts containing oxidized ore, notably in Utah and Montana, and there are also oxidized ores at other points in Arizona and a vast deposit in Chile. The treatment of such tonnages is of prime importance.

The Ajo ore has a matrix of granite with a large percentage of secondary quartz replacing feldspar. There is little calcium present in soluble form, and the oxidized ore seems to be best adapted to a leaching process. Preliminary laboratory tests showed that the ore crushed with the production of remarkably little slime and that the copper will dissolve in dilute sulphuric acid quite freely when the crushed ore contains fragments no larger than 6-mm. cubes. Tests also showed that a little cuprite is present, which is only partly soluble in sulphuric acid. There are also other soluble salts, notably salts of iron and aluminum. It was decided to investigate a leaching process for the oxidized ore, and since the ore made but little fines and could be leached with comparatively coarse crushing, we decided that we would try to leach in tanks by percolation. The amount of silver in the ore is small. Salt is apparently expensive, and it was decided that, other things being equal, the use of chlorine compounds as solvents was not desirable. I know, of course, that chlorine compounds may have a great future in leaching, but in this particular case, and in the early development of a process, it was considered that sulphuric acid offers fewer difficulties as a solvent.

To me the hydro-metallurgical problem divides itself naturally into two nearly separate divisions—the solution of the copper,

and the recovery of the copper from solution. We were obliged, however, to study the problems of solution on the basis of getting the copper into solution in the form most convenient for its ultimate recovery.

At the start we employed Stuart Croasdale to undertake a study of the solution of the copper, and we also delegated to him experimentation upon the precipitation of copper by iron. Mr. Croasdale ably conducted a long series of most valuable experiments and published a paper upon this subject which you will find in the *Transactions* of the Institute.[2] At the same time we were fortunate enough to obtain the advice of Utley Wedge upon the manufacture of sulphuric acid direct from calcining-furnace gases.

Mr. Croasdale demonstrated that the ore crushed to an 8-mm. cube, or smaller, would yield over 80 percent of its copper when treated with a dilute solution of sulphuric acid. He demonstrated that slime presented no difficulty if the ore was distributed in the tanks uniformly, and that by finer crushing 85 percent of the copper could be obtained in solution if treated for a sufficient length of time with an acid solution. He demonstrated not only that the ore was permeable uniformly, but that with comparatively small tanks the height was not a matter of great consequence, and he was easily able to use a column 12 ft. in height, and could probably use one much higher. Later on we found upward percolation preferable.

Mr. Wedge showed us that with care in calcining the sulphide fines for reverberatory furnaces at the Calumet & Arizona smelter at Douglas, sulphuric acid of 55° to 60° B. could be manufactured with a low operating cost, and a construction cost of not to exceed $3,000 per ton of daily capacity. The point of manufacture is about 300 miles, more or less, according to the route, from the mine. Mr. Wedge also undertook a study of sulphating and chloridizing roasts. His requirements were that the ore be crushed to pass a 1½-mm. screen. He showed that if the sulphide ore could be mined in parallel with the oxidized ore, and in proportion to their respective tonnages, there would be sufficient sulphur for his purposes and that a very high extraction could be obtained. He also showed that sufficient advan-

[2] Bulletin No. 82, August, 1914, pp. 1881 to 1929.

tage could not be had in using salt to offset its cost and the difficulties that might arise later. Mr. Wedge also showed that a small amount of heavy sulphides from the Bisbee mines crushed and mixed with the oxide ore would give a very high percentage of extraction after the mixture had been subjected to a sulphating roast. He also introduced the idea that a preliminary water leach would give a perfectly pure sulphate solution from which the copper could be recovered electrolytically and that the acid thus generated would be sufficient to complete the leach.

Frederick Laist in the meantime was conducting a number of experiments governing processes in a like brilliant way, and among these processes was the development of an oxidizing roast on Anaconda tailings. Like Mr. Wedge, Mr. Laist found that by calcining sulphides or mixed sulphides and oxidized ores a high percentage of the copper could be extracted by leaching. Temperature control was vastly important, as the developments of both Messrs. Wedge and Laist showed. If too high a temperature is used a large amount of the copper becomes insoluble in the strongest acid, but in both cases temperature control was demonstrated to be simple and practicable, and under these circumstances practically no insoluble copper compounds were formed. In Mr. Laist's case, however, the use of salt is essential on account of the silver contents of the charge, but he finds that it is not necessary to use this in a chloridizing roast and that a solution of salt with sulphuric acid gives him the desired extraction on the product from the oxidizing roast.

The manufacture of sulphuric acid by the chamber process, while simple, requires a very large investment, and in this case the transportation charges would amount to more than the cost of the acid. The chamber and the contact processes, of course, are the two important manufacturing processes, but even a casual study of wet methods of copper recovery shows that there are other methods of acid manufacture involving a principle similar to the chamber method, that might be used in parallel with the recovery of the copper from solution with less investment for plant and with a saving in energy that is important.

The McKay process includes a sulphating or an oxidizing roast, as he chooses, to get sulphide of copper into soluble form,

and he adopts the same process for this purpose as followed by Messrs. Wedge and Laist.

The Slater process and the Midland process deserve study. They depend upon the use of complex series of chlorides and hypochlorous compounds that will dissolve many salts of copper that sulphuric acid will not touch. They will attack, among other things, chalcocite, and they deserve serious consideration in many important but special cases, as they avoid the necessity of a preliminary roasting operation.

I regret that I am only slightly familiar with the very important work in the development of a process by E. A. Cappelen Smith for the beneficiating of the Chuquicamata ores.

Recovery of Copper from Solution.

At the beginning of our investigation we seriously considered what I called the "brutal method" of leaching, namely, the manufacture of sulphuric acid, the solution of the copper from the ore with such acid, and the precipitation of the copper by metallic iron, with the resultant complete, or nearly complete, destruction of both acid and iron and the production of an impure cement copper that will have to go through the process of smelting and refining. The results of Mr. Croasdale's tests and Mr. Wedge's cost figures indicated that such a course was commercial, and we concluded that the 1½ percent Ajo ore, with no overburden, mined by steam shovel and crushed coarse, would yield a profit on a 12c. copper market if a cheap grade of Alabama pig iron were used.

But it occurred to me, as it had occurred to many engineers, that oxide of iron could be reduced to metallic iron without fusion, and if so we might bring Bisbee sulphides to the mine, calcine them for the manufacture of sulphuric acid and then metallize the available iron in the impure calcine, already containing values requiring recovery, and use this for a precipitant. I found at the start that metallic iron was being produced by this method with an inferior fuel from high-grade iron ore by an intermittent process; that is, by first heating to the desired temperature by internal combustion of a part of the excess coal in the charge and then allowing the heated charge to stand without the admission of air, but allowing the gases formed to escape freely.

After consultation with friends, we concluded to try the experiment of a multi-hearth furnace, and at first my idea was that possibly calcining could be done on the upper hearths and the hot calcine could then pass to the lower hearths, where it could be further heated and submitted to a reducing action. We erected a small Wedge furnace, but only tried to metallize, and not to calcine in it. Some of the iron oxide was reduced to metallic iron, but on the whole our experiment was a failure because in keeping the charge hot the percentage of carbonic acid gas produced was sufficient to retard and reverse the action of carbon monoxide in reduction. In parallel with this, we also made experiments in revolving cylinders, aiming to reduce the iron to the metallic form with illuminating gas and with fuel oil by a continuous process. These also were failures.

Mr. Laist conducted similar experiments on a continuous process for making sponge iron at Anaconda, and ended with a like failure. He has, however, demonstrated that he can make sponge iron by an intermittent process in a revolving drum. It had become evident to me, even in my limited environment, that the simple use of iron, with the destruction of both iron and acid, to the production of an unfinished product, while apparently commercial, was in our extremely simple case preposterous, and investigation showed the splendid work done on other lines and convinced me that if considered from a commercial viewpoint better methods were bound to develop a process that would fit our requirements, and very much cheaper copper would result.

At the start we decided to investigate the electrolytic deposition of copper from solution, but a little later on we took up the subject of the direct precipitation of the copper by sulphurous acid gas. I prefer to attack the latter subject first for the purposes of this paper.

In the precipitation of copper by sulphurous acid gas, temperature and consequent pressure must be considered. If the copper is precipitated in metallic form this temperature and pressure are very high, but if a sub-chloride of copper would satisfy us, the temperature and pressure may be moderate. In both of these processes, the reactions we are familiar with in the formation of sulphurous acid by treating copper turnings with concentrated sulphuric acid are reversed by heat. For the pro-

duction of metallic copper the action depends upon getting sulphurous acid dissolved in the sulphate solution in sufficient amount to precipitate the copper and then heating the mixture under proper control to about 150° C. The question of the use of an abnormally rich gas is involved. Under proper regulation pure copper is produced, which only needs melting for the market, and a large excess of sulphuric acid is formed. Mr. Van Arsdale has done valuable original work on this process, followed by the work of Weidlein and others in its commercial development. Laist has studied precipitating subchloride of copper. A soluble chloride is added to the sulphate solution of copper and the proper amount of sulphurous acid is added. Moderate heat under pressure—90° C. of heat—precipitated almost all the copper as subchloride. The subsequent process of obtaining the copper without volatilization and the recovery of the chlorine offered difficulties. Messrs. Van Arsdale and Bacon have valuable experience on this subject.

These processes need further development and are most interesting. It is with no disparagement of the process that we have abandoned it in our case. I simply feel that the method would be a complicated and an expensive one, and I fear working with heat and pressure where fuel is dear and a corrosive solution is used. To me and my friends the electrolytic method seemed best adapted to our condition and the simplest and more certain of commercial application.

Of course, the first difficulty was the solution of other oxides than copper and the danger of some loss of acid thereby, and, what was more important, the susceptibility of some of these dissolved neutral salts to oxidation by nascent oxygen to the production of acid salts, which in turn will dissolve copper from the cathode. It seems that such salts are most valuable as depolarizers, but must be held under control.

After investigating the subject I advised Mr. Greenway on behalf of his company, and we employed F. L. Antisell to make and direct a series of tests and experiments covering the precipitation of copper in the presence of iron and aluminum sulphates. For some time previous I had been familiar with experiments tried by Messrs Pope and Hahn, and these gentlemen were employed to investigate in parallel the practicability of removing

enough of the iron and alumina from the solutions as they foul to keep them below the danger point in electrolytic work. Both Mr. Antisell and Messrs. Pope and Hahn began their experiments upon a laboratory scale at the Raritan Copper Works. Messrs. Pope and Hahn found the leaching could be so conducted that the rate of increase of iron and alumina was slow. They therefore decided to leach in a certain way and to treat a certain high iron and aluminum neutral solution with copper oxides by agitating, heating, and injecting air. This is a rejuvenation of the old Hoffman process applied to a new purpose. The iron and aluminum sulphates in such foul solution, together with arsenic and other impurities, are precipitated as insoluble oxides and the acid previously combined with these salts is taken over by the copper oxide and forms sulphate of copper. The clarified solution, with these impurities removed, is then mixed with the balance of the solution, thus keeping an iron content of, say, less than 0.75 percent.

Mr. Antisell began his experiments by using a patent anode. This anode was a narrow, rectangular wooden or lead frame with thin wooden sheets as diaphragms, forming a long and deep but very narrow box. It was packed with a clean coke in lumps crushed to pass a 1-in. ring, and contact was given by carbon rods imbedded in the coke. A solution of sulphate of iron and aluminum in great excess was made up and sulphuric acid added. This was used as a solvent for the copper. After the solution came from the ore it was at first passed to an absorption tower, where sulphurous acid gas was absorbed, and then it passed to the electrolytic tank. I go into no detail in describing Mr. Antisell's flow sheet and his process, as he himself is present. After promising results had been had in the laboratory tests at Raritan showing the possibility of high extraction and low power costs, Mr. Antisell sent Mr. Jamieson to Douglas, where tests were made with full-sized anodes. Excellent results were obtained here, but difficulty was had with the complete absorption of sulphurous acid. Also, the anode was cumbersome and not adapted to operating conditions, but, notwithstanding, excellent results were obtained experimentally and he ran for a long time with a recovery of nearly 2 lb. of copper per kilowatt-hour, an extraction of 80 percent of the copper contents of the ore, and

the production of nearly the theoretical amount of sulphuric acid from the SO_2 gas.

Messrs. Pope and Hahn later went to Douglas and began experiments, and also later conducted a most valuable set of experiments on the manufacture of acid-proof coatings for concrete that will neither crack nor soften under the high temperatures of the Arizona desert, and which will adhere closely to the sides of the tank. This work is very important and needs mention.

Mr. Greenway discovered that if a certain copper solution containing salts of triad elements is treated in a simple way, the iron or aluminum triad salts may be removed. Dyad salts are not affected. He was led to the belief that such oxides thus precipitated were in large part insoluble in dilute acid and that therefore he had a very simple method of removing iron and aluminum from solution. Against my prediction, laboratory tests seemed to show his contention was correct. Having used up about 300 or 400 tons of Ajo ore at Douglas for the Croasdale, Antisell, and Pope and Hahn experiments, and having promising results, the engineers moved to the mine of Ajo. Mr. Greenway erected a small plant of his own, and a Pope and Hahn plant was installed and the use of sulphurous acid was temporarily discontinued. As for the Greenway process, I am not yet at liberty to discuss it further. But I may say over 100 charges were run with this process. The iron content in the solution was kept down to less than 1 percent, and we obtained an average of slightly over 1 lb. of copper per kilowatt-hour, but the extraction was low. We then extended the time of the leach and obtained a higher extraction, and finally we began to crush the ore, which at that time had been crushed only to ½-in. ring, finer, and found that if crushed to pass ¼-in. mesh percolation was not retarded and an extraction of over 80 percent was practicable. The iron has reached as high as 1.2 percent, but we are still getting a pound of copper per kilowatt-hour from the electrolytic tanks.

These experiments have been so successful that we are proceeding with the erection of a 40-ton plant, where tanks will be used that will hold 60 tons, if necessary, and will be abundantly large to permit of a study of the comparatively even dis-

tribution of crushed ore, and we shall proceed with these most interesting experiments, using first, as we have in the smaller tanks, the Greenway process. In the meantime, the 1-ton plant will be liberated and we will immediately proceed with the continuance of a modified form of the Antisell system of leaching. He finds that with the construction of better absorption towers we can absorb the necessary amount of SO_2 gas, and he has demonstrated that with the use of SO_2 gas, using dyad iron as a depolarizer and triad iron as an oxidizer, he can manufacture sulphuric acid. We can, if successful, obtain 1½ lb., and possibly more, of copper per kilowatt-hour, and at the same time manufacture sufficient acid to replace wastage. The electrolytic copper in all cases has been fully up to the trade standards.

Conclusions.

My deductions from a study of the work of the able engineers engaged in these extensive operations are as follows:

1. Dilute sulphuric acid will give a very high extraction on oxidized ores of the Ajo type. Time is a more important element in extraction than strength of acid. A maximum size of 6-mm. cube is required. Such ore crushed to the maximum size permits percolation and the production of a clear solution because the slime content in the ore so crushed is very small.

2. Where such ore is mined at a cost of between 25c. and 50c. a ton, it is commercial on a 12c. market, even if leached with sulphuric acid and the copper precipitated with pig iron to the waste of the acid and iron and the production of an impure cement copper that requires further treatment. Metallized iron from calcines can be made and in some circumstances may prove a little cheaper than pig iron.

3. An electrolytic method for the recovery of pure copper from sulphate solutions is far preferable and will produce cheap copper. In all cases a low current density is required. Hard-lead anodes or composite anodes of hard lead and coke of uniform thickness will be used.

4. Such electrolytic method, with control of the amount of iron and aluminum in the electrolyte, and without the use of sulphurous acid gas, is practicable. An acid loss of about 1.5 lb.

per pound of copper will be sustained. Chamber acid will be required.

5. I believe there is a decided probability that the cheapest and best method will be the electrolytic deposition from sulphate solutions without iron control, and the use of the requisite quantity of sulphurous acid. The sulphurous acid will be absorbed without the tank house and in quantity that will not cause annoyance. Iron and aluminum will act both as depolarizers and catalytes. This process promises a high yield of cathode copper per unit of power and the manufacture of sufficient sulphuric acid to replace the waste.

6. While these remarks apply to the Ajo oxidized ore and ores physically and chemically similar, they need not apply to ores of a different composition. Mixed oxide and sulphide ores, be they the sulphides, chalcocite or chalcopyrite and bornite, ores containing great quantities of clay, or presenting other difficulties. have to be considered separately, and there is beyond question a great field for other processes and for other methods, both for obtaining the copper in solution and obtaining the copper from the solution.

And now, gentlemen, while thanking you for your attention, I end my theme as I began. Notwithstanding the importance of this subject, it covers but a corner in the metallurgy of one metal. There are many other subjects which if discussed in committee and with an open mind will lead to the advance of ourselves and of our institutions.

Utley Wedge, Ardmore, Pa.—It has certainly been very gratifying to hear such a comprehensive discussion of the development of the technique of leaching in connection with the property of the New Cornelia Copper Co. The presentation of this matter in the paper as read I believe to be accurate, but one aspect of the problem has not been presented. The paper relates almost exclusively to the treatment of carbonate ore. The deposit at Ajo, where this method is to be applied, comprises about twice as much sulphide ore as carbonate ore. It also comprises 1,500,000 tons of ore which is a mixture of sulphide and carbonate ore. It would be interesting to have accurate data as to the yield or percentage recovery of copper that can be

secured from the sulphide ore by the various methods of concentration. The character of the ore leads me to believe that the percentage of recovery of values from the sulphide ore by any of the wet concentration or flotation processes in use at the present time, will be materially less than the percentages which this paper has shown us it is possible to recover by a leaching process. In considering the ultimate beneficiation of this property, I would suggest that the treatment of the carbonate of copper ore should always be considered in connection with the treatment of the balance of the deposit.

Is it not true that the sulphuric acid leaching plant for carbonate ore as described, if constructed on a large scale, will have largely outlived its usefulness when one-third of the deposit of ore has been worked out? If the same facilities that will handle the carbonate ore would also handle the sulphide ore, so that the same plant and the same processes could be utilized throughout the operation, the eventual total cost of construction might be materially reduced. The leaching of carbonate ore of this character with sulphuric acid is clearly demonstrated to be a success. It is clearly demonstrated that the carbonate ore which is to be leached with sulphuric acid does not need to be finely ground to leach completely and economically. It is apparently demonstrated that with processes recently perfected SO_2 can be introduced into an impure electrolyte with advantages in economy as regards consumption of power in electrolysis and quality of product, but these advantages can largely be retained by the following operation:

Let the sulphide ore and the ore which is found between the mass of carbonate and the mass of sulphide ore, which partakes of the character of both, be ground to 20 or 30 mesh and furnaced at a temperature not much above a red heat, and the material can at once be leached with as good percentages of recovery as have been secured in the case of the carbonate ore. The copper solutions secured can be electrolyzed, and sufficient sulphuric acid can be produced from the electrolysis for use in leaching all or a portion of the carbonate ore, which methods can be identical with the methods described in the paper.

The leaching of the finely ground sulphide ore will call for somewhat modified appliances on account of the fineness of the

material, but it has been abundantly demonstrated in other plants and in other camps that finely ground material can be economically leached. There are methods of handling finely ground material in leaching which even seem to have advantages in operation as compared with the methods described for leaching material in lumps.

In case the leaching plant projected, as indicated by the paper read, is built no larger in capacity than would in any event be necessary in connection with the treatment of sulphide ore and carbonate ore by the methods indicated, then and to that extent the construction for such acid leaching of the lump material would be serviceable for the life of the property, if the construction is of such character as to last that long, and if the mining and beneficiation of the carbonate ore can be so arranged that it will extend over a like period.

I am of the opinion that sulphatizing roasting of the sulphide ore in the orebody of the New Cornelia Copper Co., coupled with the acid leaching of all or a portion of the carbonate orebody with sulphuric acid by the methods indicated in the paper, will give the lowest possible cost of operation and will give the highest possible recovery of values of any method known to the metallurgical art. This combination of methods would obviate the necessity of construction of a sulphuric acid plant; in the place of this plant there would be constructed a furnace plant for giving the required roast to the sulphide ore. At the start, with only carbonate ore accessible, enough of the carbonate ore could be roasted mixed with small percentages of iron pyrite from neighboring camps to sulphatize the carbonate of copper.

I believe the cost of a roasting plant for conducting the process in this way is amply justified by the large recovery of values which can be made, and I believe that the advantages of this combination of methods are so great that the beneficiation of this property by such methods would yield several million dollars in excess of what would be secured if the sulphide ore were treated by any of the known concentrating processes followed by the smelting of the concentrate.

As a general statement, the class of copper ores known as oxidized ores and carbonate ores, to the extent that they are free from alkaline earths or other gangue materials that are

readily attacked by sulphuric acid, will, in general, lend themselves to the treatment that Dr. Ricketts has described: namely, the treatment with sulphuric acid. But the past history of the leaching method as applied to the metallurgy of copper is full of instances where efforts have been made to accomplish results by leaching processes not preceded by the study which was given to this matter in connection with the New Cornelia operation. Such attempts in the past have justified the criticism of leaching processes which was once made in a general way by the father of a gentleman whom I see present, who said that the chief thing he had against leaching processes was that they were so like *eine Schweinerei.* If I am asked to give the English equivalent of that, I would say that it is apparent that the installation of leaching processes which the German gentleman has seen did not appeal to his esthetic sense.

But another day is very rapidly approaching, and the advance that has been made in the past few years in this line of progress seems to me to be revolutionary. There is so much being done by so many different companies that the efforts of any individual in connection with such practice must seem small.

The connection that I have had with this matter had led me to emphasize especially the effort to secure pure solutions which would yield to electrolysis without difficulty; and the development which has been brought about by two gentlemen who will be heard from this evening makes it seem probable that solutions quite impure in character will hereafter be economically electrolyzed. I regard the work of these gentlemen as of the utmost importance. The application of leaching processes to copper ores and copper calcines is practiced on a larger scale than is generally known. Over 1,000,000 tons yearly are treated for the extraction of copper by leaching. The largest leaching operation in the world is one operation which treats about 750,000 tons per annum. I refer to the Rio Tinto Co. The process used by the Rio Tinto Co. is in its essential character a sulphatizing roasting process. The ore is piled up in heaps 30 ft. deep, which are called *terreras,* and the ore is allowed to heat by chemical action until a sulphatizing roasting condition is produced and sulphates of copper are formed, which are leached out. The balance of the leaching of copper ores, done on a large scale

throughout the world, is mostly chloridizing leaching, where salt is used. The leaching process with salt is very extensively carried out in Germany and England. There are several hundred thousand tons, I think, chloridized every year in Germany and England. I know individually of quite a number of very large operations there with which I have come in contact in connection with the installation of furnaces for chloridizing roasting. There is a very considerable tonnage chloridized in this country. The chloridizing process is familiar to a great many here. For the benefit of the others, I will say that in general, ore, which has previously been roasted to deprive it of most of its sulphur, down to a point where the sulphur is from one and one-quarter to one and one-half times the copper content, is mixed with a percentage of salt, usually in good practice in the neighborhood of 10 percent, and this mixture, which is reduced to a fineness of 3 mm. by grinding, is then heated in chloridizing furnaces to a dull red temperature, or even slightly below, and the copper is chloridized and subsequently leached out with water, and with such hydrochloric acid as is caught in the scrubbing towers in connection with the furnaces.

The use of sulphur dioxide in connection with the precipitation of copper is a matter which personally I have been watching with very great interest. The quantity of sulphur gas which is escaping from the different smelter plants in this country is so prodigious that it seems like a waste; it seems as if this material will eventually be utilized and turned to some account. It is very possible that to some extent this will be brought about in connection with either the electrolytic or other precipitation of copper, where sulphur dioxide is evidently going to be very much in demand. There has been a possibility, if not a probability, that liquid SO_2 might be required in this connection. It is interesting to note that at the present time, as far as I know, there is no liquid SO_2 plant in the United States. There are several in Germany, and one or two in England, and the stoppage of the importation of liquid SO_2 from Germany has advanced the price to about 10c. a pound at the present time. This certainly does not look attractive as a metallurgical proposition, but the possibilities of the cheap production of liquid SO_2 to

permit of its being shipped considerable distances for use, are such that I think it will come to pass in this country in a comparatively short time.

E. A. CAPPELEN SMITH, New York, N. Y.[3]—Our plant is practically finished; the leaching plant itself, as well as the mining plant, is practically completed. We have been slightly delayed with the completion of the power plant on account of the war in Europe—our power plant is being manufactured in Germany; according to our present plans, we expect to have the plant in operation by the first of April. So far in the construction work everything has gone on very nicely, and it now remains only to start the plant.

The general plan of work consists in steam-shovel mining the copper deposit followed by leaching the ore. From the crushing plant the ore will be moved by a belt and unloaded by a bridge that straddles the leaching tanks. The leaching tanks—six large concrete vats set end to end—are each 160 ft. long, 110 ft. wide, and 16 ft. deep. Each tank is designed to hold 10,000 tons of ore. After the ore has been delivered to these by the traveling bridge from the main belt, the first solution is applied, by upward displacement. At first we had planned to conduct the operation entirely by downward percolation, but we found a slight tendency of the finer material to clog the filter bottom; also, we found that channels were formed in the charge. These difficulties were entirely overcome when we instituted the method of applying the liquor by upward displacement. The first treatment solution stands on the ore for 48 hr. This solution is immediately followed by the washing liquors in rotation run on the top of the ore, and displacing the previous solution by the piston method. In this way, we find that we can wash the ore so that the tailing will contain only from 0.015 to 0.03 percent soluble copper. We think this is about the limit, and we can obtain this result without introducing any more water in the process than sufficient to make up for that carried off in the tailing as moisture, and in the solution which is discarded to get rid of the surplus acid produced from the ore.

The solution is removed from the tanks through lead-lined

[3] Compare Transactions Am. Electrochem. Soc., **25**, 193 (1914), article on Copper Leaching at Chuquicamata, Chili.

iron pipes, and conducted to a central pumping station, where we will use centrifugal lead-lined pumps, each with a capacity of 5,500 gal. per minute against a lifting height of 62 ft. The pumps have been built by the Worthington company; they have been tested in the manufacturers' shops, and as far as we can tell they are going to be highly satisfactory.

The solution is then delivered to the storage tanks, placed at an elevation above the leaching tanks, and from there it flows by gravity to the plant where we are going to eliminate the chlorine. We propose to pass the solution through cylinders 30 ft. long and 4 ft. in diameter, half filled with shot copper. By this means, the chlorine is precipitated in the form of cuprous chloride. The operation is continuous. The mixture of precipitated cuprous chloride, with the copper sulphate solution containing about 3 percent sulphuric acid, is run into Dorr thickeners, where the precipitate is separated from the solution. The cuprous chloride pulp corresponds to between 1 and 2 percent of the total amount of the solution. We are installing some Kelly filter presses, which are lead lined, and we are also going to install an Oliver filter, likewise lead lined, in order to compare the two types.

The filter-pressed material will be delivered to the smelter by the usual methods, and at the smelter it will be mixed with limestone and coke finely crushed (8- to 10-mesh material), put through a pug mill, pressed into briquets, and delivered to the blast furnace. In the blast furnace will be produced copper, and calcium chloride as a slag. The copper will be taken to a small reverberatory furnace, where it will be granulated and again used in the dechlorinators. We find that on account of the oxidizing agents present in the solution, partly in the form of ferric sulphate and partly in the form of nitric acid, the efficiency of the copper shot is only about 50 percent of the theoretical; in other words, there is a direct solvent action on the metallic copper in addition to that caused by the reduction of the cuprous chloride. Practically all of the copper produced in the form of cuprous chloride will go back into the process.

The solution, after the chlorine is removed, is fed by gravity into the electrolytic tanks with a strength of approximately 5 percent copper. It will run through the depositing tanks, ar-

ranged in sections of 16 tanks each, which will have about 13,000 amperes to a tank. The voltage will be about 2.3. We expect a yield of approximately 1 lb. of copper per kilowatt-hour. The solution will leave the last tank containing about 1.5 percent copper. We find that the current efficiency remains high down to about 1.5 percent copper; if we go lower than that, the current efficiency will drop off rapidly. By holding to these limits we will have an ampere efficiency of approximately 90 percent. The solution from the last tank in the cascade will be delivered back to the leaching plant to be used over again.

Our problem is somewhat unusual in this respect, that we have available sulphuric acid present in our mineral, and instead of having to look around for means of producing acid, we have to look for a method of getting rid of the surplus sulphuric acid. We will have to dispose of a quantity of the solution on account of its content of sulphuric acid.

There are no soluble impurities in the ore itself, such as antimony and arsenic. Soluble lime and alumina and alkali salts are negligible. Consequently, the usual trouble experienced in connection with leaching processes is not present in our problem. Chlorine, which we have in the upper part of the ore body, was really our most annoying difficulty, but the treatment of the solution with metallic copper has eliminated this difficulty. In addition to this, we also have a small amount of nitric acid in the form of nitrates. So far we have not been able to determine that any especial difficulty arises in the process itself from the presence of nitric acid. It has, however, a rather deleterious effect on lead connections, lead pipes, and lead anodes. We have noticed, however, that this action occurs only at points where we are handling the strong solutions—those containing 8, 9, or 10 percent sulphuric acid. Nitric acid is present up to 0.8 percent, but outside of the difficulty mentioned, it does not give any trouble. Its presence does not seem to have any particular function in the process itself, and we have not been able to determine that its being there causes any lower current efficiency. It does not seem to have any effect on the voltage.

Chlorine seems to have a tendency, which was to be expected, of lumping the deposit to a certain extent, and the use of colloids to prevent this does not seem to be very encouraging. I

think it will be a question, more than anything else, of watching the deposit, and perhaps not allowing the cathode to get quite as thick as in ordinary practice.

Underlying the large oxidized ore body, at present developed to the extent of 200,000,000 tons, we have a sulphide ore body. Small-scale tests conducted on this material show that it can be treated either by roasting and leaching, or by water concentration followed by smelting in the usual manner. This ore body is also of enormous extent, but details have not as yet been decided upon for the final working of it, as the 200,000,000 tons of oxidized ore already developed will keep us busy for some time to come.

George D. Van Arsdale, New York, N. Y.—During the last few years we have been doing considerable experimenting on methods of precipitating copper. The first patent on precipitating from sulphate solutions by heating with SO_2 under pressure was taken out by us (U. S. Pat. 723,949).

This reaction, $CuSO_4 + SO_2 + 2H_2O = Cu + 2H_2SO_4$, is interesting, but there are a number of practical difficulties which will be met with in carrying it out on a scale of any size, the main ones being that it is not easy to get a sufficiently strong solution of SO_2 to carry out the reaction, and that the design of an apparatus for heating large amounts of corrosive solutions under pressure is a considerable problem. If these can be overcome, I believe the process may be developed, but I agree with Dr. Ricketts' opinion that electrolytic methods of precipitation are preferable.

Regarding our work at Douglas, we have felt that to say much about it was a little premature, as experiments are still in progress, but some notes on the preliminary experiments may be of some interest.

The general method which we adopted for the tests was sulphatizing roasting, leaching, and electrolysis from sulphate solutions, using depolarization.

The reason for the consideration of the sulphatizing roasting was that the materials which we have to treat contain in most cases large amounts of soluble alumina, and therefore, with a regenerative process only, we would be almost sure to have a

deficiency of acid. With the sulphatizing roasting this deficiency of acid would be more or less made up.

The plant used for the preliminary experiments consisted of a 20-ft. six-hearth Wedge muffle furnace, several small leaching tanks, in an electrolytic installation designed to precipitate about 250 lb. of copper a day.

The objects of the roasting experiments were to determine the capacity of the furnace, the fuel consumption, and the percentage of extraction, both water soluble and acid soluble. The objects of the electrolytic experiments were to determine the power and the ampere efficiency, to determine whether the anodes, which our preliminary experiments seemed to indicate, would be satisfactory under working conditions, and also to determine the best methods of dissolving and applying the SO_2 gas.

The results of our roasting experiments were as follows: We roasted three principal classes of material, in which the average insoluble copper in the calcines was 0.11, 0.16, and 0.41. The water-soluble copper showed 70 percent of the copper contents, 40 percent and 51 percent, respectively, and the total extraction was 92.9, 88.0, and 70 percent. One of the principal results of these experiments was to show us that for this class of roasting it was necessary to have more or less fine crushing as a preliminary.

The results of our preliminary electrolytic experiments were fairly satisfactory. We obtained a total amount of copper precipitated of something over 2 tons at an average figure for power of about 1.6 lb. of copper per kilowatt-hour. We produced acid per kilowatt-hour equivalent to about 5.1 lb. The ampere efficiency was low. This, however, was due to several reasons not directly connected with the process. We had a large number of short-circuits and other troubles, but we felt quite sure at the end of these preliminary experiments that we should get about 2 lb. of copper per kilowatt-hour. We had, however, a certain number of uncertainties and some anomalous results, so we started some further experiments on details of solution and other matters.

The further experiments resulted in the following general conclusions:

First, that it was not necessary to have such a large amount of SO_2 in solution as we had previously thought, and that, in addition, much better results could be obtained by using SO_2 together with iron, rather than either one alone. In other words, the function of the SO_2 was not only to act as a depolarizer, but also to act chemically in keeping the iron reduced. We also found there was a certain favorable effect from a high aluminum content. The temperature increase is favorable in the same way as in copper refining. With iron salts present there is a decreased ampere efficiency with increased temperature. This was counteracted by SO_2 and by increased current density.

As a result of these further experiments, we laid down the conditions of high ferrous sulphate in solution, high alumina, a temperature of about 115° to 130° F., current density of about 15 amperes per square inch, and sufficient sulphur dioxide present to reduce the voltage, and maintained sufficiently to keep the iron in the ferrous condition, and under these conditions I expect it will be possible to get a yield of from 2 to 2.5 lb. of copper per kilowatt-hour.

As to "foul solutions," which has heretofore seemed to be the principal bugbear in electrolysis, as long as the iron can be kept in the ferrous state, which can be done by SO_2, it is fairly safe to say that, up to certain limits, better results will be obtained from so-called foul solutions than from pure copper sulphate solution.

We are now about to start a 75-ton plant, in which we expect to apply the information which we have gained to the treatment of one class of ore, and the result of the work which will be done in that plant will no doubt be published later.

Raymond F. Bacon, Pittsburgh, Pa.—We have been in the field of copper investigation for some time, as many others have, but we feel it is somewhat premature to say very much as yet. We have been working on several different lines, and we believe no one leaching process will be developed that would be applicable to all ores or all conditions. There are certain leaching processes which are better adapted to the conditions of certain ores, and other processes are better adapted to the conditions of other ores.

As regards electrolytic processes, I think a good deal of the

work we have been doing has been pretty well covered in different ways by the statements which have been made here tonight. Our work on electrolytic processes has been along two lines. First, to ascertain the optimum conditions for the electrolytic precipitation of copper from sulphate solutions obtained by the leaching of oxidized copper ores. In this phase of the work I may say that we finally obtained conditions under which we ran a solution over the ore through the precipitating tanks and then over the ore again, 20 cycles being completed, without any purification of the solution. There was precipitated on the average in these 20 cycles 1.86 lb. of copper per kilowatt-hour, and the current efficiency on the twentieth cycle was fully as good as that on the first cycle. Our second line of work on electrolytic processes has been an attempt to find efficient and cheap depolarizers, so as to increase the amount of copper precipitated by a definite amount of electrical energy. We have found one very cheap substance which for short runs gave us 4 lb. copper per kilowatt-hour.

In regard to the sulphur dioxide process, we have been actuated by this thought: it is necessary in most ores to have quite an excess of acid to take care of mechanical losses and to take care of alkaline substances in the ore. One way of doing this is along the line which has been spoken of—by using the sulphur dioxide in an electrolytic cell. We, also, have used sulphur dioxide in an electrolytic cell, but all of our work has tended to show that the efficiency of sulphur dioxide as an anode depolarizer in a sulphate solution is rather low. Because of this low efficiency our calculations showed us that it is cheaper to precipitate directly with the sulphur dioxide under pressure than to use the sulphur dioxide as an aid to electrical precipitation; that is, the heat required for direct precipitation with sulphur dioxide will be cheaper in most localities than the electrical energy required either for straight electrical precipitation or for the combination in which sulphur dioxide assists the current. We all appreciate the advantage which any electrolytic process has of giving directly cathodes of electrolytic copper. On the other hand, it has seemed to us that for most localities and most conditions the disadvantages of electrolytic processes, as at present developed, outweigh this advantage. Some of the disadvan-

tages of electrolytic processes are these: The fouling of solutions immediately and seriously cuts down the current efficiency. Changes in the character of the ore, particularly as regards soluble impurities, are always to be expected in large ore bodies. The electrolytic process is very sensitive to changes thus brought about in the electrolyte. The installation and upkeep costs of the electrolytic precipitation process are very high, and to obtain efficiency requires constant supervision by high-priced men. One rather fundamental objection to electrolytic processes has not been discussed here tonight. In electrolytic processes, at least of the type which has been spoken of tonight, the copper content of the electrolyte can be reduced in the precipitation cells no lower than 1.5 percent copper. That means that it is not easy so to conduct a cycle of leaching, precipitation, etc., that all of the water-soluble copper shall be removed from the ore and the volume of the solution in the cycle shall be kept constant. For example, let us assume in a systematic leaching process that all the copper has been extracted from a ton of ore and that that ore is then in contact with the solution which in the cycle is strongest in acid, having just come from the precipitation tanks, and which, of necessity, still contains 1.5 percent of copper. This one ton of ore is drained as thoroughly as possible and, according to our experience, then contains from 40 to 100 gal. of this solution containing 1.5 percent copper. In other words, there is from 6 to 13½ lb. of copper still in this ore. By adding the proper amount of wash water to retain the volume of solution in the cycle constant—that is, in this particular case, from 40 to 100 gal. of wash water—the copper content of that ore will be reduced to from 3 to about 7 lb. To wash out further this soluble copper, so as to have a negligible quantity of soluble copper remaining in the ore, according to our experience, requires an amount of wash water such as to increase very appreciably the total volume of solution which is in the cycle. It is obvious that in any process in which there is practically complete precipitation of the copper, as in Weidlein's sulphur dioxide process, this washing difficulty does not arise. In place of losing soluble copper in the ore, one there loses a corresponding amount of sulphuric acid; and in Weidlein's process sufficient sulphuric acid is constantly being formed, so

that this loss can be taken care of. As to the element of danger in processes in which a solution is heated under pressure, I would call your attention to the fact that there are thousands of boilers operating continuously in the United States under pressures considerably in excess of those used in the Weidlein process. We built in Nevada a 40-ton plant, and we have had certain mechanical difficulties, as we expected to have. These difficulties we are meeting by the installation of a continuous process of precipitation. The advantages of continuous precipitation will be evident to all mill men. Our expectation that the cost of heat in this process of precipitating pure copper is less than the cost of electricity for electrical precipitation has been borne out. Of course, I recognize that there are localities where electrical power is so cheap that an electrolytic precipitation process should be the one to be considered, but I believe that for most localities in the western United States some of these other processes are more favorable as regards cost. In the Weidlein process a very large excess of acid is constantly regenerated, and all who have had experience in the leaching of ores know how desirable this is. In that connection I will say that we have developed a system of handling sulphur dioxide and a method of concentrating it from dilute flue gases. We believe we have made noteworthy progress in that direction, but I am not prepared at this time to go any further into that. In a short time we will be able to say a little more on the subject.

Frederick J. Pope, New Rochelle, N. Y.—The investigations in connection with the leaching of copper ores to which I will refer were carried on by A. W. Hahn and myself. In our preliminary work we were assisted by Messrs. Bryan and Aldrich, of the Raritan Copper Works.

In our first consideration of the work, we had to decide: The solvent we would use; how we would precipitate the copper from the solution, and what we would do with the iron in the electrolyte. Without going into the details of the reasons, we decycle. It is obvious that in any process in which there is prac- and that we would recover the copper from the solutions by electrodeposition. As to how we would take care of the iron in the electrolyte, we had to choose between controlling the iron

(*i. e.,* keeping it in the ferrous state) in the solution and eliminating it from the solution. The removal of the iron appeared to offer the more attractive field.

Briefly, the method followed involves leaching with sulphuric acid, removing a portion of the iron from the solution, and precipitating the copper electrolytically.

Regarding the leaching *per se,* I do not think I could say anything which would be of any particular interest. There are certain factors which govern the extraction of copper from an ore, and when these factors are given due consideration, I think we can get about the same extraction with one process as with another.

In considering how to remove iron from the electrolyte, we were reminded of the work which had been done by Hoffman at Argentine, where he precipitated iron from bluestone solution. Hoffman accomplished this by heating the solution in a suitable tank, agitating with air, and adding copper in an oxidized form. I think he used a roasted lead-copper matte. This work of Hoffman's gave us our idea for the removal of iron from the solution.

For the copper oxide necessary in this work we have used high-grade copper carbonate ore, oxide formed by the roasting of cement copper, roasted high-grade sulphide ore, also roasted copper sulphide concentrates. In our demonstration plant (10 tons daily capacity of carbonate ores) we used roasted concentrates. The concentrates were roasted in a small Wedge furnace, the results obtained being far better than those attained in our preliminary work when we roasted the same class of concentrates in a laboratory muffle furnace.

In order to obtain a satisfactory reaction between the copper oxide and the iron, etc., in the solution, it is imperative to have the oxide material very finely divided. The roasted concentrates we used were ground in a small Abbé mill. We found that with 5 or 6 hr. grinding we obtained a product 93 percent of which would go through a 200-mesh screen. It is probable if we had had time to investigate this grinding operation, we would have found that it was not necessary to grind for 5 hr., but, owing to the shortness of the period at our disposal for securing results, we did not have the opportunity to bring this operation down to the shortest time limit.

From the Ajo carbonate ore we removed a little more than 2 lb. of iron per ton of ore treated. In order to keep the iron in the solution below the percentage deleterious to electrical efficiency, it was necessary to treat approximately one-quarter of the solution. We found that by manipulating the solution going on and off the ore in a certain way we could concentrate a large proportion of the iron in a certain part of the solution. This was accomplished as follows: The first solution going on the ore carried about 2.5 percent of free acid and was kept on the ore by circulating until it was approximately neutral. This neutralizing precipitated from the solution on the ore a considerable proportion of the iron, alumina, etc. This neutral solution was drawn from the ore, and after acidification by electrolyte coming off the electrolytic tanks, was sent to electrolytic tanks for precipitation of the copper. As the first solution was withdrawn from the leach, it was replaced by fresh solution. This fresh acid solution not only removed some more of the iron from the ore, but also picked up the iron which had been precipitated from the first solution used. This second solution, now high in iron, was circulated until it was nearly neutral, when it was replaced by fresh solution carrying 4 to 4.5 percent free acid, which completed the leach. The total leaching period averaged about 80 hr. The solution high in iron, etc., was sent to that part of the plant where removal of iron and other impurities was accomplished.

In purifying the solution, it was first heated to 195° to 200° F. When this temperature was attained, agitation with air was begun and the finely ground oxide material was gradually added. Maintenance of a temperature of about 195° F. and agitation with air was continued for 3.5 hr. During the first hour all the ferric iron was precipitated. The removal of the ferrous iron was slower and we found that it was not advisable to endeavor to precipitate it all. In 3.5 hr. we easily precipitated 90 percent of the total iron and at the same time removed 65 to 75 percent of the alumina, 50 percent of the manganese and all of the arsenic, antimony and bismuth which might be present.

After the above operation the pulp was passed through a Schreiber wooden filter press. The solution came out beautifully clear and was sent to the high-acid electrolytic circulation system. We anticipated that with the precipitate produced we might

have trouble with the filter cake; that it would be slimy and difficult to handle. We did not find it so. The cakes were 2 in. thick, firm, washed well, and the amount of copper in the form of unused oxide they contained was well within commercial limits.

As you are well aware, when the iron sulphate, aluminum sulphate, etc., react in the agitation tank with the copper oxide, they give up their acid radicals to the copper, forming copper sulphate, which in the electrolytic tanks yields sulphuric acid, so that the only loss of acid is that due to combination with the alkalies and that due to loss by entrainment in the tailing. This acid loss we found we could easily replace by a proper control of the roasting of the concentrates in the Wedge furnace; *i. e.*, we could so control the roast as to maintain in the calcine sufficient copper sulphate either as water-soluble sulphate or as basic sulphate to compensate for the acid losses to which I have referred.

Regarding the electrolytic part of the work, we simply followed standard tank-house, liberator-tank practice. Our anodes were antimonial lead, 4.0 percent antimony. We tried both grids and sheets. With the grids our voltage was 0.3 volt higher than with the sheet anode, and we discarded the grids in favor of the sheets.

With reference to the use of a lead anode, I might say we commenced our work with some apprehension, fearing that there might be a serious loss of lead. We made a number of protracted tests, and as a result we calculated that the cost for lead anodes at Ajo with lead at 8c. per pound would be less than 0.2c. per ton of ore treated.

In the process I have outlined there is really nothing new or novel. It simply consists of an idea picked up here and another there, and the putting of these various ideas together.

If we were to criticise the process, the pros and cons might be summed up about as follows:

Advantages:

a. Simplicity.

b. Every step in the process has been in use in commercial plants for years.

c. Saturated solutions avoided.

d. Wash water not excessive, and if it should become so, it can be taken care of.

e. Impurities which would injure the quality of the electrolytic copper are eliminated from the electrolyte.

f. Acid control very simple.

g. No step in the process is dependent upon fine adjustments.

Disadvantages:

a. High and low acids used. This necessitates more solution-storage tanks, more solution lines and more pumps than if a single solution were used.

b. There is an extra operation: namely, purification of electrolyte, which involves the installation of a roasting furnace, boilers, compressor and filter press.

c. The lead anodes will probably have to be changed at the end of four or five months, since the lead peroxide scale formed will increase the voltage.

J. Parke Channing, New York, N. Y.—The problem presented in the Miami district is a little different from that in the districts referred to in the discussion of this evening, inasmuch as the ore to be treated there is one which is a mixed chalcocite and carbonate. The gangue, as you know, is particularly free from any impurities that go into solution, but the fact that both chalcocite and carbonate are present makes it a rather difficult problem. The particular ore deposit upon which we worked was that of the New Keystone, but the same class of ore existed in the Miami, and also on the Inspiration. The problem therefore presented to us was a straight leaching one, which would have to be proceeded with by complete dead roasting, or else it would be a mixed process, water concentration followed by leaching, or possibly leaching followed by water concentration; and then finally, if flotation came in, we might have to make three bites of the cherry—that is, use water concentration, flotation and leaching. You can readily see there would be a great many combinations, and whether it would be desirable to leach first, then water concentrate, and then float, or whether it might be desirable to make the sequence different, we do not know. This Keystone ore averages about 2¼ percent copper, of which anywhere from 30 to 40 percent is oxidized. After making a number of concentration tests we decided upon attempting a dead

roast; in other words, converting all to the copper into a soluble form and leaching it.

It is not possible for me to give you the details of the numerous different things we tried. I may say, however, that, for the purpose of precipitation, we tried the electrolytic method. The problem with respect to these mixed ores is by no means solved, and we are still conducting experiments along these lines, and I think Mr. Canby, the gentleman in charge of the experiments, can give you in a general way some idea of what we have accomplished and what is still left undone.

R. C. Canby, Wallingford, Conn.—The only thing I can think of which has not been mentioned is the circulation of the electrolyte. In our electrolytic work I designed the cells so that the solution, instead of flowing lengthwise against the flat surfaces of the anodes and cathodes, flowed crosswise of the cell. In that way, in the use of sulphurous acid gas, I had hoped, by having a rapid circulation, to use a much smaller quantitiy of both copper and the depolarizing elements in the electrolyte, with a correspondingly stronger current, and also to be able to precipitate the copper without heating the electrolyte. I was able to use a current density as high as 10 or 12 amperes per square foot with the temperature of the electrolyte about 18° to 20° C., and get a very satisfactory coherent deposit. I think that was the only novelty in the electrolytic work.

The other things were done very much along the lines which have been discussed here this evening. We think, however, it would be very much better if all of the oxides could be treated in the present plant, and we are now working to that end, so as not to have a separate installation of the semioxidized ores. It is along that line that experiments are now being carried on, so as to treat the oxidized material, which is mostly in the flotation tailings. I think there were perhaps five or six different methods of manipulation tried, such as leaching resulting slimes and leaching before crushing for concentration, etc., but all of these combinations contained really nothing of any special interest, as they are thoroughly familiar to everybody.

J. Parke Channing.—How about roasting with the oil furnace—would that be of interest?

R. C. Canby.—That might be of interest. The problem was to use our 14° Baumé fuel oil, to be burned at a temperature of 2,000°, and yet keep our ore bed at not to exceed 800° to 1,000° C. I accomplished this by using a furnace similar to that used for the Huntington and Heberlein process at El Paso and at three other American smelting plants, the hearth revolving past the flame, so that I was able to roast the ore without at any time bringing the temperature of the roasting ore above the desired 1,000° C., whereas the fuel was being burned at about 2,000°, or a little over. The furnace was entirely of reinforced concrete construction and stood well.

Richard Lamb, New York, N. Y.—During 1907 I designed and erected a leaching and electrolytic copper extraction plant at High Hill, Va., on the Virginia Copper Co's property, to treat the bornite and chalcocite ores found there.

The average ore analyzed about as follows:

	Percent
Copper	3.0
Sulphur	1.5
Silica	89.0
Lime	0.75
Iron	1.5
Magnesia	3.0
Alumina	0.35

Owing to the large percentage of silica, this ore is difficult to concentrate economically. The large bulk of silica crowds off the values on any form of concentrating apparatus, and at least 50 percent of the values is lost if machines are worked at a speed necessary to make them efficient. There is a large body of copper ore in the Virginia copper belt, but many failures have been made in the attempt to concentrate it. However, the ore is ideal for leaching. The magnesia and alumina are mostly in silicate form, and do not go into the acid solution, and the large percentage of silica is in its favor when leaching.

I built the first experimental plant for treating this ore in Hoboken, and first tested leaching the ore in open tanks. In crushing this ore to, say, 10 mesh, at least 25 percent goes into slime. This adds to the difficulty of leaching if the usual leaching tanks are used. I therefore substituted a chlorination barrel for the leaching tank, in order that the crushed ore might be stirred while leaching. Stirring arms in open leaching tanks

when using sulphuric acid disintegrate quickly. The lead-lined barrel used stirs the ore without injury from the acid. As the ore is a sulphide, it has to be roasted. In the Hoboken test plant I used a small Brückner roaster. In the large test plant at the Virginia Copper Co's mine I used an Edwards roaster, with a capacity of 30 tons of ore per 24 hr. I was able with this roaster to control the heat. While we had only 1.5 percent of iron in the ore, to avoid its polluting the electrolyte I sought to change it from an oxide to a sesquioxide of iron, which is insoluble in dilute sulphuric acid, by keeping the heat while roasting to about 900° F. Dr. James Douglas told me that he had succeeded in changing the iron to a sesquioxide of iron in a copper ore he was leaching, having over 25 percent of iron in same, by roasting with the proper degree of heat. I found that if the ore is crushed only to a size that exposes the sulphide on the surface, the roast will be as good as it would be if the ore was ground exceedingly fine. There is some oxide and carbonate of copper ore in the form of cuprite, malachite, melaconite and green carbonate produced, but these are not separated when coming out of the mine, so they were sent to the roaster, although the roasting was superfluous, as sulphurous acid will take the copper of those oxide and carbonate ores into solution without their being roasted. The ideal roast would be to change the sulphide ores into sulphate, but since this condition would require careful manipulating, I sought to make the sulphide ore oxide and sulphate, but not to make a sweet roast, only seeking to leave as little of the ore in a sulphide condition as possible. If the ore could all be roasted to a sulphate condition, the sulphur of the ore would go into the solution while leaching and thus add sulphur to the acid supply.

The ore, ground to 10 mesh and roasted, was put into a lead-lined barrel. A solution of sulphurous acid was made by burning sulphur in an inclosed oven with a supply of air sufficient in volume to supply the oxygen to produce sulphurous gas, and under a pressure just sufficient to overcome the hydraulic head due to the height of the water from the submerged outlet of the sulphurous gas delivery pipe to the surface of the water in the tank. The water is acidulated to about 10° Baumé by absorbing the sulphurous gas.

This acid is pumped into the leaching barrel with the roasted ore, and the barrel is revolved until the copper has gone into solution. This takes about 3 hr. Compressed air is then passed into the barrel and the solvent is forced from the barrel through the filter in same. This filter is the same as is used in the barrels used in chlorination work. This solution entered a 20,000-gal. cypress stock tank, painted with Mogul acid-proof paint. The elevation of the tank was such that gravity would produce a flow of the solution or electrolyte from the stock tank through 16 lead-lined cypress vats, placed at elevations with reference to each other so as to continue the flow of the electrolyte through the 16 vats. An acid-proof pipe line was also provided, situated below the vats, so that any vat could be discharged or shunted. Each tank was provided with ⅛-in. thick lead anodes and cathodes, with exposed surface 25 by 36 in., in all 1,030, the cathodes providing over 6,000 sq. ft. of depositing surface. An overhead crane was provided to carry the anodes and cathodes to their respective places.

The electric current was supplied by two Holtzer-Cabot 30-volt, 1,200-ampere generators, with a 120-volt, 1.5-kw. exciter.

By the use of sulphurous acid the anodes were prevented from peroxidizing. The sulphurous acid of this electrolyte is changed to sulphuric acid by the electrolysis and becomes a stable acid. After passing through the vats any loss of acid from being neutralized by the alkali of the ore is replaced by sulphurous acid, as described, and the electrolyte is used over and over again to leach more ore. When the electrolyte becomes polluted it is run into a larger vat having an extra number of electrodes, so that the current density is very slight and the copper is practically depleted. The electrolyte from this hospital tank can be run to waste or further treated for its sulphur contents.

The voltage supplied to each tank was 1.8, and a current density of 3 amperes per square foot was used. The electrolyte was permitted to run from 0.25 to 0.5 percent in copper when used over for further leaching.

The output was 30.6 lb. of pure electrolytic copper per horsepower-day of 24 hr. With water power at $12 per horsepower per year, this would represent a cost of 0.12c. per pound for electrolytic treatment.

With steam power costing $48 per horsepower per year, the cost for electrolytic treatment would be about ½c. per pound of copper produced. Producing copper in the Virginia copper belt, from underground to finished product, would cost about 6.9c. per pound, working upon a scale of, say, 5 tons of copper per day. In my belief, using the large available water power nearby, and making 5,000 tons per year, the cost of copper will not exceed 6c. per pound. The capacity of the trial plant described was 2,800 lb. per 24 hr. In building this plant I was employed by one man, who alone, on the advice of his brother, an experienced metallurgist, undertook to lease the Virginia Copper Co's mine and put up the experimental plant. The plant was run only a few days, the owner having lost his money in the fall of 1907, and the plant was thrown into the courts, with disastrous results to the owner. Enough was done to demonstrate that, with the above-described combination of well-known and tried-out apparatus, using the cheapest of solvents, sulphurous acid, there is no reason why a suitable copper ore should not be treated on a large scale, so as to produce electrolytic copper at a lower cost than by the old dry-process methods.

DISCUSSION AT ATLANTIC CITY, APRIL 23, 1915.

Lawrence Addicks: It seems to me that the general field of leaching sulphide ores without a prior roasting is not very promising. I have been particularly interested in work along these lines, and it appears conclusive that wet concentration including flotation, followed by the usual smelting method is more economical than attempting to roast and to leach such ores. This is due primarily to the fact that it is very difficult to carry out a sulphatizing or oxidizing roast which will afford a higher extraction of dilute sulphuric acid than eighty percent of the copper contents, whereas it seems assured by concentration, flotation and smelting we can recover 90 percent. Also we need the sulphur dioxide gas readily obtained from the roasting of concentrates for the manufacture of sulphuric acid, either directly or indirectly, with sulphate leaching.

Roasting lead sulphide ores direct naturally requires extraneous fuel, and does not give a flue gas sufficiently concentrated in SO_2 to be of any service. We are, therefore, practically driven to the consideration of at least rough concentration to get concentrates for the production of acid and tailings which may be treated either in wet way or by flotation. The latter process, however, seems to have easily the advantage, always speaking, however, of straight sulphides.

If we consider oxidized ores, however, where the conditions are favorable as to the absence of serious quantities of acid-consuming bases and of silver and gold values, it seems clear that the leaching processes have come to stay. We have several experiments now being carried out on a large scale on such deposits, and these will doubtless develop the mechanical side of leaching in such a way that we can predict with a good deal more security just how far such methods can be applied on more doubtful ground.

The question of partially oxidized ores where considerable sulphides are still present and the ores carry paying quantities of silver and gold, even though oxidized, is still debatable territory. Just at present the pendulum is swinging strongly in the direction of flotation, and without doubt it will travel too far and the leaching man can well afford to catch it on the rebound rather than struggle with it on the way out.

Perhaps the most interesting possibility is flotation recovery of nearly all of the values from a sulphide ore, and then applying leaching methods to the concentrates so produced, in competition with smelting.

As to the mechanics of leaching, a tremendous amount of work is now being done in several fields, and apparently both downward and upward percolation are being satisfactorily applied to coarse ore, and there are also adaptations of cyanide machinery to fine material. I have been personally supervising a trial of modified Dorr thickeners on concentrator slimes tailings, and it seems quite clear that the use of such apparatus is entirely practical.

As to precipitation, the general tendency seems to be toward electrolytic methods. Of course, scrap iron is out of the question in a plant of any size, because there will not be sufficient

of such material available in a given district, and we are driven to the importation of pig iron which may be taken as worth around $20 a ton in most Western districts. Then we have sponge iron produced from concentrates which, however, fouls the cement with its silica and other gangue constituents. Of course, silver and gold, if we are using solutions in which they are soluble, are precipitated with the copper in the cement.

President Lidbury asked me to say a word about the electrolytic experiments we have been making at Douglas. I am not in a position today to give details regarding this work, but hope to be able to do something in the way of a formal paper later. I may say, however, a few words in a general way. I took up this work a year ago where Mr. Van Arsdale laid it down, and at that time he had all but demonstrated the practicability of using carbon anodes in sulphate solutions provided some sort of efficient depolarization was employed. While I still do not like to make a positive statement regarding the durability of such anodes, I can say that our work during the past year has practically convinced me that they will not deteriorate, provided the depolarization is effective—in other words, the oxygen suppressed. We have been using Acheson graphite in the work so far, and I do not know whether or not this will apply to compressed carbon.

In the early work sulphur dioxide gas was used directly in the cells as a depolarizer. That is, however, open to three serious objections: first, it creates an abominable atmosphere in the cell room; second, it is prodigal in the use of sulphur dioxide; and third, it is difficult to get sufficient concentration of this gas in the liquors, since its solubility depends upon the partial pressure of the SO_2 in the flue gases, and we are limited to a relatively weak gas and further handicapped by the altitude at most Western mining camps. We have, therefore, substituted ferrous sulphate as a depolarizing agent, reducing it outside of the cell room from the ferric state to which it is transformed at the anode by the use of the sulphur oxide gas. Now, of course, ferric sulphate is a strong solvent for metallic copper, and heretofore those attempting the use of iron salt as a depolarizer have been obliged to resort to a diaphragm to protect the cathode, and a diaphragm is a curse to any process.

I have always believed that the best way to attack a problem was to find out what the enemies to success were, and endeavor to make friends of them. Our enemies in this case were the quantities of iron and alumina which accumulated in the solution, which have led most experimenters to devote a great deal of time to methods of removing them.

By using iron sulphate as a depolarizer we have welcomed iron as an ally, and we have further found that aluminum sulphate present in considerable concentration acts as a strong sedative in the cell and greatly reduces the speed of reaction between the ferric sulphate and the cathode proper. Just when that happens there I do not know, but the practical results are that we are able to carry sufficient iron in the electrolyte to form an effective depolarizer and yet prevent a serious attack on the cathode without the use of any troublesome diaphragm.

It is necessary to use quite violent agitation in order to secure thorough depolarization, and this is done by means of compressed air. We are, therefore, able to figure on a working voltage in the neighborhood of 0.8, and as we hope to work at about 80 percent current efficiency, it is evident that between two and three pounds (0.9 to 1.4 kg.) per kilowatt-hour should be recovered. Of course, the violent agitation makes a magnificent deposit. You can see from this sample which I will hand around that the cathode looks like a piece of rolled copper. We have found about 13.5 amperes per square foot (148 per sq. m.) a practical density for our conditions when carrying the recovery at about 115° F. (46° C.).

J. V. N. Dorr: Copper leaching is usually approached from the viewpoint of the laboratory, so that the chemical side of it is more in evidence than the mechanical. I have had occasion to realize their importance in endeavoring to furnish apparatus to meet the mechanical problems involved.

Three steps may be considered: first, dissolving the copper; second, separation of the cuprous solution from the tailing; third, precipitating the copper from solution.

The best method of dissolving the copper will depend largely on the fineness of crushing required to make economic extraction. If satisfactory solution can be obtained at three-eighths mesh or

coarser, direct percolation seems simplest. If it requires grinding to between that point and forty mesh, leaching by slow passage through a series of Dorr Classifiers with counter-current washing has proved successful, but requires separate treatment for the overflowing slime. If finer grinding is needed, continuous agitation with countercurrent washing to expose nearly extracted material to fresh acid, is advisable.

In many cases where settling is bad, filtration seems advisable but a considerable loss in acid and dissolved copper can be allowed to avoid filtration of acid liquids in large scale work.

In all three cases the recovery of the dissolved copper is almost simultaneous with its solution, as it is difficult to finish the latter until the former is well advanced.

The counter-current washing system has proved so successful in cyaniding that its application to copper leaching seems certain. It allows the recovery of a very high percentage of the dissolved copper in a highly concentrated solution. Where electrolytic work is contemplated and rich solutions are to be kept in circulation it appears essential to precipitate a portion of the copper by iron. Acid-proof machines have been produced successfully for leaching, agitating and thickening.

LAWRENCE ADDICKS: I really haven't anything to say, except regarding the speculating I have been doing as to what might be the cause of so many of these things which we see happening. One of our propositions in connection with the work of electrolysis of solutions from leaching is to take the ferric sulphate and reduce it by SO_2 to form free sulphuric acid. SO_2 is a pretty strong reducing agent and should make a thorough reduction directly to ferrous sulphate; however, we do not get an immediate reduction, but some intermediate products first. After the ferric sulphate is formed, the mixture is still green. It is a very pale green. After it is reduced it is pretty good blue, and we put SO_2 in and get a brilliant grass green, and it stays so for some time, several hours. When the solution is in this green condition, if we dip a slip of bright copper into the solution it blackens up with a precipitate of copper sulphide, which would mean that there are reduction products higher in sulphur, and the reduction is completed in the case of the copper with pre-

cipitation of copper sulphide. We have not really found any explanation for it, and that is what I meant by saying that our experiments were not advanced sufficiently for us to give you the results now.

F. C. FRARY: What happens if you leach an ore containing chryscolla and try to electrolyze that solution? What becomes of the silica? Does it go to the cathode with the alumina?

LAWRENCE ADDICKS: We have not been dealing with any straight copper silicate, but, as I remember, it goes into solution with the liberation of silica. That, of course, has to be removed by some form of settling or filtration. It makes no trouble. That is what they are doing in Butte. They are simply leaching with sulphuric acid; putting in acid and treating it in tanks without filtration of any kind. I never saw mention that they had any trouble due to silica. It probably stays with the gangue in the original leaching of the ore.

JOS. W. RICHARDS: In this connection I understand that the Chile Exploration Company is using the fused magnetite anodes which they expect to get from Germany, but it is a question as to whether their supply is not entirely cut off, therefore the use of an unattackable anode other than this magnetite anode is just at present of very great interest.

I would suggest that an anode plate might be built up similar to the negative plate of a storage battery. It need not be reversed, of course, but would always act as anode, and perhaps therefore be permanent as an unattackable anode in these sulphate solutions.

PRESIDENT LIDBURY: What kind of a plate?

J. W. RICHARDS: Like the per-oxide plate of the storage battery.

PRESIDENT LIDBURY: Made of what?

JOS. W. RICHARDS: Made up with a lead grid and lead dioxide, compressed.

A paper presented at the Twenty-seventh General Meeting of the American Electrochemical Society, in Philadelphia, April 24, 1915, at a Joint Session with the American Electroplaters' Society, President F. A. Lidbury in the Chair.

ELECTROPLATING WITH COBALT.[1]

By Herbert T. Kalmus, C. H. Harper and W. L. Savell.

In 1842, Professor Boettger pointed out that dense and lustrous electro-deposits of nickel could be obtained, which, on account of their resistance to oxidation, great hardness and elegant appearance, were capable of many applications. The outcome of this has been that during the last 20 years commercial plating with nickel has developed to an industry of great magnitude. On the other hand, no platings of cobalt or of its alloys have ever been in extended commercial use. No doubt part of the reason is because of the difficulty of obtaining a supply of metallic cobalt at an attractive price. On the other hand, for commercial plating, where labor, overhead charges, the preparation of the surface to be plated, the difficulty of maintaining the bath, the amount of buffing, the current efficiency, and particularly the speed with which the work may be run through the baths, influence so greatly the cost of the finished work, the price of the metal to make up the anodes and the salts is by no means alone the determining factor in the choice of that metal. Moreover the speed of depositing largely determines the hardness and other physical properties of the plate, which in turn determines the weight of metal required for satisfactory commercial tests.

A great many technical points in connection with the plating of cobalt have not been investigated, but the corresponding investigations for nickel have been comparatively thorough.

[1] Authors' abstract of report under the above title to the Canadian Department of Mines, published by permission of the Director of Mines, Ottawa, Canada.

This publication is one of a series on the general investigations of the metal cobalt and its alloys, particularly with reference to finding increased commercial use for them. These are being conducted at the School of Mining, Queen's University, Kingston, Ontario, for the Mines Branch, Canadian Department of Mines.

This paper presents a large amount of experimental data on cobalt plating. It attempts to record data, to summarize, and to draw conclusions about practical cobalt plating and its application in the industries. Theoretical considerations concerning the explanation of the results are reserved for a separate publication.

Before platers can adopt cobalt for many purposes, on a considerable scale, a number of questions must be definitely answered by experiments, such as:

I. Can cobalt be plated on iron, steel, brass, tin, German silver, lead, etc., in such manner as to yield as uniform, as adhesive, and as satisfactory a finished surface as nickel?

II. Is cobalt plate harder than nickel plate?

III. Is cobalt plate less corroded than nickel plate by ordinary atmospheric action?

IV. What bath is most suitable for the deposition of cobalt, when a heavy protective coating, which may be buffed to a superior finish, is required to be deposited in a minimum of time?

V. Can a satisfactory cobalt bath be maintained at such an increased concentration as compared with the nickel bath, that plating from it may proceed with greater speed?

VI. Is the cobalt bath more or less troublesome than the nickel bath as regards crystallization, etc.?

VII. Should alkali, acid, or neutral baths be used for cobalt plating?

VIII. Is the nature of the deposit improved by hardeners such as boric acid, citric acid, magnesium salts, etc.?

IX. How does the maximum current density at which cobalt may be deposited commercially compare with the maximum current densities used in the commercial deposition of nickel?

X. What electromotive force had best be used for cobalt plating, using the bath found most suitable for a given class of work?

XI. How do cobalt anodes compare with nickel anodes as regards solubility, under the conditions of the plating bath?

XII. What are the relative current efficiencies of cobalt and nickel plating under the best conditions?

XIII. How do the electrical conductivities of satisfactory cobalt and nickel plating solutions compare?

XIV. Can cobalt be deposited to considerable thicknesses from any solution in commercial practice?

XV. What are the relative costs of cobalt and nickel plating?

Although numerous statements have been published in the past with regard to cobalt plating, the conclusions to be drawn

from a survey of the existing literature and patents would lead one to be very skeptical as to the advantages of cobalt plating over nickel plating. It is noticeable, however, that the conditions for the production of good cobalt plates, as given by different authors, vary tremendously among themselves. Not only are the conclusions often diametrically opposite, but likewise the data from which these conclusions are drawn.

Considering merely the question of the relative maximum current densities with which cobalt and nickel may be successfully plated, there is little or nothing in the literature relating to such solutions of cobalt which we have found in this laboratory to be most suitable for fast plating. If it can be shown to be practically feasible to plate cobalt from a bath at several times the speed that this is possible for nickel, other things being equal or in favor of the cobalt, this greater speed of turning out the work, with attendant economies, might offset a very considerable difference in the initial cost of the anodes and salts of the two metals. If cobalt-ammonium sulphate, because of its very much higher solubility than nickel-ammonium sulphate, or for other reasons, may be used as a plating bath at very much higher current densities than is used in nickel baths, the plater might turn out cobalt plate more economically than nickel plate. Moreover plating at greater speed means a harder and denser plate with consequent less weight of metal required.

A large number of plating experiments were undertaken at this laboratory with a view to studying the questions outlined above. Numerous types of cobalt baths were used and various concentrations of each solution. The object of this paper is to set forth the data of these experiments and the conclusions to be drawn therefrom.

The following paragraph shows briefly the wide variance of opinion to be found in the most important contributions to this subject in the literature.

LITERATURE ON ELECTRODEPOSITION OF COBALT.

Langbein, in his well-known work, "Electro-deposition of Metals" devotes nearly one hundred and seventy-five pages to the deposition of nickel, and a scant two pages to the deposition of cobalt. With regard to cobalt, Langbein remarks as

follows[3]: "For plating with cobalt, the baths given under 'Nickeling' may be used by substituting for the nickel salt a corresponding quantity of cobalt salt. By observing the rules given for nickeling, the operation proceeds with ease. Anodes of metallic cobalt are to be used in place of nickel anodes.

"Nickel being cheaper and its color somewhat whiter, electroplating with cobalt is but little practiced. On account of the greater solubility of cobalt in dilute sulphuric acid, it is, however, under all circumstances to be preferred for facing valuable copper plates for printing.

"According to the more or less careful adjustments of such plates in the press, the facing in some places is more or less attacked, and it may be desired to remove the coating and make a fresh deposit. For this purpose Gaiffe has proposed the use of cobalt in place of nickel, because the former dissolves slowly but completely in dilute sulphuric acid. He recommends a solution of one part of chloride of cobalt in ten of water. The solution is to be neutralized with aqua ammonia, and the plates are to be electroplated with the use of a moderate current."

From our experiments we find in general that the substitution of cobalt for nickel in Langbein's baths, as recommended by him, does not do justice to the metal cobalt. These baths have been primarily worked out for nickel, whereas cobalt, being in many instances of far greater solubility, requires a much more concentrated bath than that recommended, for the fastest and best plating. Some of our best cobalt solutions are not included at all in Langbein's list.

MacMillan[4], Watt[5] and others, report that cobalt deposits are harder than the corresponding nickel deposits. Brochet[6] says: "Cobalting has been proposed in place of nickeling when a deposit of greatest hardness is desired."

On the other hand Langbein[7], Wahl[8] and others say that cobalt plates are softer than the corresponding nickel ones.

S. P. Thompson[9] finds that articles plated with cobalt are less

[3] "Electro-Deposition of Metals," Langbein, 6th Edition Revised, Henry Carey Baird and Co., Philadelphia, p. 318.
[4] Electro-Metallurgy, MacMillan, 1901, p. 227.
[5] Electro-plating and Electro-refining of Metals, Watt-Phillips, 1902, p. 360.
[6] Manuel Pratique de Galvanoplastie, 1908, p. 313.
[7] Electro-plating of Metals, 6th Edition, p. 319.
[8] Electro-plating and Electro-refining of Metals, Watt-Phillips, 1902, p.360.
[9] Journal of Institute of Electrical Engineers, 1892, p. 561.

corroded in the atmosphere of London than either silver or nickel plate, while Stolba[10] reports that cobalt salts treated like nickel salts yield metallic deposits of a steel gray color, less lustrous than nickel and more liable to tarnish.

While some authorities report that it is practically impossible to obtain a deposit of cobalt more than a few hundredths of a millimeter in thickness, Bouant[11] says: "Electrolytic deposits of cobalt are easily obtained even of a very great thickness, so that electrodeposition of cobalt is as easy as that of copper."

A review of much of the literature on the electrodeposition of cobalt was presented at the meeting of the American Electrochemical Society, at Atlantic City in April, 1913, by O. P. Watts. A consideration of Watts' paper emphasizes the diversity of opinion with regard to cobalt plating above mentioned.

Watts mentions about fifty solutions of cobalt which have been used with greater or less success. Some of these are similar to ones used by us in our experiments, but several of our best solutions are not included in the list.

Many of these baths are recommended only for very weak currents, others are more or less indefinite, and there is much contradiction among them. For example, the first solution in Watts' list is: "Becquerel's solution, 37.5 grams of cobalt chloride neutralized by ammonia or potassium hydroxide, gives a brilliant, white, hard and brittle deposit. A very weak current must be used." Later, quoting from Watts, Isaac Adams says in a patent application: "I have found that a solution made and used in the manner described in the books will not produce such a continuous and uniform deposit of cobalt as is necessary for the successful and practical electroplating of metals with cobalt. . . . I have found further that the simple salts of cobalt, such as are recommended by Becquerel and others, are not such salts as could be used in practical electroplating with cobalt. . . . "

Even in a matter so immediate and important to the practical plater as the acidity or basicity of his plating bath, there is no general agreement among the authorities even for nickel solu-

[10] Electrical Review, Nov. 18, 1887, p. 503.
[11] La Galvanoplastie, Bouant, 1894, p. 294.

tions, much less for cobalt. Dr. Langbein[12] writes: "All nickel baths work best when they possess a neutral or slightly acid reaction . . . an alkaline reaction of nickel baths is absolutely detrimental, such baths deposit a metal dull and with yellowish color and do not yield thick deposits." Bennett, Kenny and Dugliss, in a paper read before the American Electrochemical Society at New York City, April 1914, state as two of their seven general conclusions the following: "A good deposit of nickel may be obtained from the double sulphate if the solution at the surface of the cathode is kept alkaline. . . . Since alkalinity is necessary for good efficiency, it is very probable that in acid solutions nickel is deposited only when impoverishment of the hydrogen ions has caused the solution to become alkaline and given the conditions under which nickel may deposit."

These are but a few of many contradictory statements to be found in the literature.

SUBDIVISION AND ARRANGEMENT OF EXPERIMENTS.

A very large number of plating experiments were conducted by us at this laboratory for the purposes outlined above, in connection with which some sixteen different types of solution or baths were employed and studied. Following is the list:

Series I—Simple cobalt-ammonium sulphate.
" II—Cobalt-ammonium sulphate with an excess of ammonium sulphate.
" III—Cobalt-ammonium sulphate with an excess of ammonium sulphate, to which is added citric acid.
" IV—Cobalt-ammonium sulphate with ammonium chloride.
" V—Cobalt chloride with ammonium chloride.
" VI—Cobalt-ammonium sulphate with boric acid.
" VII—Cobalt-ammonium sulphate, cobalt carbonate, and boric acid.
" VIII—Cobalt sulphate, potassium citrate, and ammonium chloride.
" IX—Cobalt phosphate with sodium pyro-phosphate.

[12] Electro-Deposition of Metals, Dr. Geo. Langbein, 6th Edition, Revised, p. 251.

Series X—Cobalt-ammonium sulphate with magnesium sulphate.

" XI—Cobalt sulphate, neutral ammonium tartrate, with the addition of tannic acid.

" XII—Cobalt sulphate, potassium tartrate, and tartaric acid.

" XIII—Cobalt sulphate, sodium chloride, and boric acid.

" XIV—Cobalt sulphate, ammonium sulphate, magnesium sulphate with boric acid.

" XV—Cobalt-ethyl sulphate, sodium sulphate, and ammonium chloride.

" XVI—Cobalt sulphate, ammonium sulphate, ammonium chloride, and boric acid.

Each set of plating experiments with a definite group of principal components in the bath has been given a series number. Variations in concentration of this bath, or changes in the relative proportions of the components in the bath, have been designated by the use of subscript letters, A, B, and C, etc. This subscript notation has also been used to include minor changes and additions to a bath. Also, where a nickel bath has been used analogous to a given cobalt bath, the data for the experiments on it are noted under the corresponding cobalt series. For example, Series III refers to baths of cobalt sulphate, ammonium sulphate, and citric acid. A combination of these was called III A, whereas the same bath with a small amount of sodium sulphite, to note its effect, was called III B, and the same bath, substituting 34.5 grams of nickel sulphate for the 34.5 grams of cobalt sulphate in bath III A, was called bath III C. In this way all the modifications of a bath are grouped under one series.

METHOD AND ARRANGEMENT FOR PLATING EXPERIMENTS.

There were two distinct series of plating experiments, one set conducted at the plating department of the Russell Motor Car Co., Toronto, and one set at this laboratory. The next few paragraphs refer to the latter.

Arrangement of Electrical Circuit: Power was taken from three storage batteries connected in series, yielding approximately six volts. The various baths were connected independently across the six volt terminals of this storage battery set, with appro-

priate resistance in series with each. In this way the potential across the electrodes of each was cut down to the desired value. A five-volt Weston voltmeter, reading to 0.01 volt, was connected directly across the electrodes of each bath. A Weston milliammeter, 600 milli-ampere scale, was connected in series with each bath.

Plating Tank and Computation of Effective Electrode Surface: The plating tanks used for these experiments were of glass, rectangular in shape, and of approximately the following internal dimensions: 12 x 6 x 6 inches (30 x 15 x 15 cm.). Some of them were deeper than this.

In general, if the bath is not large in cross-section in comparison with the area of the electrodes, the results obtained will not be reproducible. We tried experiments using a tank not much larger in cross-section than the electrodes. In that case the voltage required for a given current density, with electrodes 10 cm. apart, is very much greater than with a tank of considerably larger cross-section, other conditions being the same. This is largely due to the fact that with the smaller cross-section of tank the available solution between the electrodes is diminished.

For the most part, our electrodes were approximately 3 x 2 inches (7.5 x 5 cm.) in surface, placed from 10 to 20 cm. apart, in the centre of the rectangular plating tank above mentioned. If the electrodes were kept in place, the tank lowered away from them and replaced by a very large tank of the same solution, we found that the electromotive force across the electrodes for a given current density diminished by nearly 20 percent. The leads of the electrodes were coated with a layer of insulating asphaltum, as described in the paragraph on electrodes. In the case of these experiments, therefore, the effective electrode area is something like 20 percent less than the exposed surface.

Instead of submerging electrodes of the above size in the middle of the tank, in some of our experiments the electrodes were lowered into a tank to such a depth as to be just covered by the solution. It is obvious, in this case, as we found by test, that the electromotive force across the electrodes would diminish if the height of the bath around them be raised. This is true even though no greater area of electrode is thereby covered with

solution, and although the leads are insulated with asphaltum. The reason is that with the level of solution just covering the top of the electrodes, the electrical field between the upper portion of the electrodes was limited by the surface of electrolyte, as compared with what it would be with the electrodes immersed in the centre of a large body of electrolyte. Consequently, had our experiments been performed in an ideally large tank, the electromotive forces would have been smaller for the same current densities. We preferred to use a bath approximating to the conditions of plating practice, and have in all cases noted in the tables to follow the values of current density, electromotive force, etc., just as observed without correction.

Good practice for commercial nickel plating with many solutions, is to have about eight gallons (36 liters) of solution for each square foot (11 sq. dm.) of anode surface. In our experiments we have not departed widely from this value, although we find different solutions require a somewhat different ratio for the best results.

Plating Experiments: The plating experiment itself consisted in noting changes in appearance of the solution and electrodes as the deposition progressed, as well as making a record of milliammeter, voltmeter and time readings at frequent intervals. The concentration of the bath was measured from time to time, and the physical properties of the resulting plate were studied.

Wherever current efficiencies were desired, milliammeter readings were made at intervals of not more than two minutes. These readings were very constant in all cases, so that more frequent readings were not necessary. Also the cathode was carefully dried and weighed before and after the deposition. Conditions of weighing of the electrode before plating and after plating were made identical.

Advantage was taken of the well-known fact for the deposition of nickel and other metals, that the deposit is more adhesive when started at a higher potential than is to be used throughout the greater part of the plating run. Our practice was to diminish the resistance in series with the bath, so that an initial electromotive force of about six volts was used, sending very considerable currents through the bath during approxi-

mately the first thirty seconds of the run. The effect of this was uniformly satisfactory in causing the plating to adhere firmly.

After a sufficient plate had been deposited on the cathode, it was removed from the bath, immediately washed in cold water, and then rinsed in boiling water until it came to a uniform temperature, after which it was dried in hot saw-dust. This procedure was practiced throughout the plating experiments.

Buffing and Finishing Cobalt Plates: The cathode, after being removed from the plating bath and dried, is in general white and metallic, and requires but little buffing to produce a satisfactory mirror surface. Our practice has been to employ a large buffing wheel rotating at high speed, which will "color" the work in one operation. Cobalt plates color more readily than nickel and for commercial purposes should not require cutting with tripoli, etc.

Preparation and Use of Anodes: Both cast and rolled anodes were used for these experiments, the cobalt employed analyzing as follows:

	H-218	H-219	H-209	H-221
Co	95.70	98.00	98.75	95.63
Ni	0.80	0.75	nil	0.75
Fe	2.10	1.35	1.35	3.72
As	....	....	nil	0.048
S	0.043	0.042	0.0052	0.029
C	0.040	0.060	0.052	0.052
P	0.004	0.007	0.0067	0.005
Si	0.050	0.067	....	....

H-218: 2 cast anodes, 3½ x 2 x ¼ inches (9 x 5 x 0.6 cm.)
H-219: 4 cast anodes, 3½ x 2 x ¼ inches (9 x 5 x 0.6 cm.)
H-209: 6 anodes, 7 x 2½ inches (18 x 6.4 cm.)
H-221: 4 rolled anodes, 3½ x 2 x ¼ inches (9 x 5 x 0.6 cm.)

The cast anodes were poured in sand and smoothed down with an emery wheel to a finished surface of approximately 3½ x 2 x ¼ inches (9 x 5 x 0.6 cm.).

The rolled anodes were made from ingots about 8 inches (20 cm.) in length, and 1 square inch (6.25 sq. cm. in cross-section, which were rolled down to plates of ¼ inch (0.6 cm.) thickness, from which anodes 3½ x 2 x ¼ inches (9 x 5 x 0.6 cm.) were finished.

Impurities in Anodes: Nickel anodes, as sold in the market, frequently contain in the neighborhood of 92 percent nickel and 7½ to 8 percent iron. The iron is cast in the anode because

pure nickel is not corroded rapidly enough under most conditions to furnish the necessary metal to the bath. Iron is a cheap material and has a solution tension enough greater than nickel to make it effective for the end in view. The greater solution tension of cobalt in the plating baths, as compared with nickel, renders practicable the use of a lesser amount of iron, or no iron at all. Very pure cobalt anodes are readily dissolved, under the conditions of many of our best plating tests. The freedom of the cobalt anode from iron no doubt has much to do with the diminished corrosion of the cobalt plating as compared with the nickel plate. This will be discussed further on in the paper.

Rolled vs. Cast Anodes: Cast anodes of both nickel and cobalt dissolve much more readily than the rolled anodes. With a number of each in a nickel or cobalt bath, the proportion between the two may be so chosen that the composition of the electrolyte remains constant as the anode goes into solution. If too large a proportion of cast anodes is used, the anode dissolves with too great readiness and the bath may become alkaline. Conversely, if too large a proportion of rolled anodes is used, the solution of the anode may not take place with sufficient readiness, and the bath may become acid and depleted in metal. The greater solubility of cobalt anodes in a number of the plating baths described in this paper, as compared with nickel anodes in the corresponding nickel bath, renders the use of a larger proportion of rolled anodes possible in the case of cobalt than is customary at present with nickel in the nickel-plating trade. The greater solubility of the cobalt anode is distinctly in its favor for practical plating purposes.

Cathodes: The cathodes for these experiments were of brass, iron and steel, and were usually 3½ x 2 x ¼ inches (9 x 5 x 0.6 cm.) in dimension. One side of the cathode was given a high polish with emery and buffing wheels, and the other was covered with a thin coat of asphaltum varnish.

It is of the utmost importance in all plating work that the cathode be absolutely smooth and thoroughly cleansed from particles of dust, grease, etc. This was accomplished by the following procedure: Brass, steel or other stock as required, was

first machined down to the required size, after which they were smoothed down with an emery wheel and finished with an appropriate buffing wheel to a mirror surface. This left the surface with a certain amount of grease and adherent buffing material, which was removed by scrubbing with "Kalye" caustic solution. After thorough rinsing with water, the electrode was immersed in dilute hydrochloric acid, or in dilute potassium cyanide solution, and again thoroughly rinsed with water. It was then ready for use in the bath.

In addition to smooth plain cathodes, a number of them were prepared by cutting patterns and depressions on one side. These were used in the same manner as the smooth ones after cleansing and buffing as described.

Preparation of Salts: The ammonium sulphate, ammonium chloride, boric acid, citric acid, potassium citrate, tannic acid, sodium sulphite, sodium phosphate, ammonium tartrate, and magnesium sulphate used for these experiments were Merck's chemically pure, purchased from a supply house, as were also the reagents used in the preparation of the cobalt salts.

All cobalt compounds used for these experiments were prepared at this laboratory.

The Solubility of Cobalt and Nickel Salts: The relative solubilities of cobalt sulphate and nickel sulphate, and of cobalt-ammonium-sulphate and nickel-ammonium-sulphate are important in considering the greater conductivities of the cobalt solutions as compared with the corresponding ones of nickel. These solubilities are considered later when discussing the greater speed of cobalt plating and the saturation concentration of some of the baths employed, so that a brief table of solubilities at room temperature is given herewith:

SOLUBILITY TABLE.

Grams of Salt Dissolved by one liter of Water.

	Comey[13]	Kraut[14]	This Laboratory
$CoSO_4$, anhydrous, 23°C.	362	380	362.2
$NiSO_4$, anhydrous, 23°C.	405	379	363
$Co(NH_4)_2(SO_4)_2$, anhydrous, 23°C.	171	171	164
$Ni(NH_4)_2(SO_4)_2$, anhydrous, 23°C.	66	66	72.8

[13] A Dictionary of Chemical Solubilities, A. M. Comey (MacMillan and Co., 1896).
[14] Gmelin: Kraut's Handbuch der anorganischen Chemie, Vol. V, Sect. 1 (1909).

The salts actually used in making up the solutions were $CoSO_4.7H_2O$, $NiSO_4.7H_2O$, $CoSO_4.(NH_4)_2SO_4.6H_2O$, and $NiSO_4.(NH_4)_2SO_4.6H_2O$.

From the above table it is apparent that the solubilities of cobalt and nickel sulphate are not very different. These, however, do not lend themselves to satisfactory plating solutions without adding various other compounds to them. On the other hand, cobalt ammonium sulphate is approximately 2.5 times as soluble as nickel-ammonium sulphate. As will be shown by our experiments, the saturated solution of this cobalt-ammonium sulphate offers an extremely rapid and satisfactory plating bath.

Ageing Tests: With all the plating baths which were found to be satisfactory or promising, both ageing and efficiency tests were run. The ageing tests were for the purpose of ascertaining the constancy of the bath during continued use for plating over a considerably longer period than was necessary for our experiments. The solution was analyzed for cobalt content and tested for acidity and alkalinity at intervals of 15 hours during plating runs of one hundred or more hours' duration. This was in addition to the series of runs already made with the given bath, operating with it to produce the plates studied. The result of these ageing tests are given with each set of experiments.

Efficiency Tests: Efficiency tests were made in the usual manner by carefully weighing the quantity of metal deposited in a measured time and comparing it with the theoretical amount of metal which should have been deposited in accordance with Faraday's Laws. The data for these tests are given for each important solution in its appropriate place, after the plating and ageing tests.

Current Densities: Unless specifically stated to the contrary, the current densities given in the tables to follow and throughout the text are cathode current densities, computed by dividing the total current by the cathode area.

An approximate notion of the anode current density may be obtained from the following statement, although it is impossible to compute it with any degree of accuracy. At the beginning of each experiment, the anode was smooth and of approximately the same area as the cathode (see page 85), but as the experiment

proceeded, the anode gradually increased in effective area, due to unequal corrosion of its surface. At the end of some of our experiments the anode area may have been more than twice that of the cathode.

In our conclusions and through the text of this paper we speak of allowable current densities with the various solutions, and we recommend certain ranges of current density which are permissible for the best plates. In every case these are cathode current densities, but are, of course, only valid with a sufficient anode area. We have conducted our experiments under conditions which might be called good standard practice for plating shops, which means, so far as anode area is concerned, that the anode area was in every case greater than, and in many cases twice, that of the cathode area.

Complete Details: Full details of experiments with solutions of all the sixteen series are to be printed in Bulletin No. —, 1915, Canada Dept. of Mines, Ottawa. The present paper contains those for solutions I B and XIII B only, the compositions of which are given on pages 91 and 100.

DATA OF PLATING EXPERIMENTS WITH SOLUTION I B.

CAST ANODES

Reference No. of Experiment	Current Density		Electromotive Force, Volts	Electrode Distance, cms.	Cathode Area, Sq. cm.	Duration of Plating.	
	Amp. per Sq. dm.	Amp. per Sq. ft.				Hr.	Min.
1.	0.75	7.0	1.0	17	37.1	1	30
2.	1.0	9.3	1.5	19	37.1	1	30
3.	1.0	9.3	1.5	24	23.7	1	0
4.	1.0	9.3	1.70	19	23.7	2	0
5.	1.2	11.2	1.95	19	37.1	1	0

1. Cathode brass. Bright, uniform, glossy plate, which required but little buffing to give a satisfactory surface.

2. Cathode brass. Plate same as No. 1.

3. Cathode brass, with grooved channels to afford high and low spots. A good, smooth bright plate obtained over entire surface. When cobalt plate was dissolved off in nitric acid, grooves lost their plate first, showing thinner deposit there than on higher places.

4. Cathode brass. Very satisfactory plate, hard, bright and easily buffed.

5. Cathode brass. Bright, uniform, glossy plate, which required but little buffing to give a satisfactory surface.

Data of Plating Experiments, Solution I B—Continued.

CAST ANODES.

Reference No. of Experiment	Current Density		Electromotive Force, Volts	Electrode Distance, cms.	Cathode Area, Sq. cm.	Duration of Plating.	
	Amp. per Sq. dm.	Amp. per Sq. ft.				Hr.	Min.
6.	1.2	11.2	1.7	24	23.7	1	0
7.	1.5	13.9	2.05	24	23.7	2	0
8.	1.5	13.9	1.20	10	37.1	1	30
9.	1.5	13.9	2.1	16	37.1	1	30
10.	1.7	15.8	2.4	24	23.7	1	15
11.	1.8	16.8	2.55	24	23.7	2	45
12.	2.0	18.6	2.85	24	28.0	2	15
13.	2.2	20.5	3.35	24	27.3	1	30
14.	2.5	23.3	3.75	24	25.0	2	45
15.	2.7	25.1	2.25	23	22.2	1	15
16.	3.5	32.6	3.0	22	20.0	1	30
17.	4.0	37.2	2.9	20	18.0	1	0
18.	4.5	41.8	4.9	20	27.5	1	30
19.	4.5	41.8	3.0	10	27.5	1	30
20.	4.5	41.8	2.95	10	27.5	1	0

6. Cathode brass, with grooved channels to afford high and low spots. A beautiful smooth plate obtained over entire surface. High and low spots evenly coated.

7. Cathode same as 6. This plate was very smooth and bright on removal from bath, and after slight buffing assumed a beautiful finish. Uniform in thickness on high and low spots. Thickness of plate 0.062 mm.

8. Cathode a polished steel knife. A bright, smooth, hard, even, satisfactory deposit.

9. Cathode same as 8. Beautiful, bright, smooth plate, easily buffed to mirror surface.

10. Cathode brass, with grooved channels to afford high and low spots. This plate was very smooth and bright on removal from bath, and after slight buffing assumed a beautiful finish. Uniform in thickness on high and low spots.

11. Cathode same as 10. Plating the same.

12. Cathode same as 10. A beautiful white, hard lustrous plate obtained, with no sign of burning or scaling.

13. Cathode same as 10. Plating same as 12.

14. A very smooth, even, hard plate, white in color, which after slightly buffing assumed beautiful satisfactory finish.

15. Same. No signs of burning.

16. Cathode brass, with grooved channels to afford high and low spots. Very smooth, even, hard plate, white in color, which after very slight buffing assumed beautiful satisfactory finish. No signs of burning.

17. Cathode same as 16. Plating same.

18. Cathode brass. Plate fairly uniform and bright, but darkened at edges. Began to peel at one corner.

19. Cathode brass. Plate similar to last experiment, with burning slightly marked, but no peeling.

20. Cathode brass. Plate similar to previous ones, but burning not quite so marked. Buffed satisfactorily, but showed slightly pitted, due to gas bubbles.

Data of Plating Experiments, Solution I B—Continued.

ROLLED ANODES

Reference No. of Experiment	Current Density		Electromotive Force, Volts	Electrode Distance, cms.	Cathode Area, Sq. cm.	Duration of Plating.	
	Amp. per Sq. dm.	Amp. per Sq. ft.				Hr.	Min.
21.	0.39	3.6	0.44	10	26.2	2	0
22.	0.61	5.6	0.55	10	26.7	2	0
23.	1.0	9.3	1.6	16	37.0	24	0
24.	1.0	9.3	0.77	10	27.0	1	0
25.	1.5	13.9	2.2	16	37.0	16	0
26.	2.0	18.6	1.30	10	26.5	0	45
27.	3.0	27.9	1.32	10	20.0	0	20
28.	4.0	37.2	1.35	10	11.7	0	15
29.	4.0	37.2	1.35	10	11.7	0	25
30.	4.25	39.5	4.25	20	27.0	1	15
31.	4.5	41.8	4.60	18	27.0	1	0

21. Cathode brass. Smooth, uniform, white plate, readily buffed to mirror surface.

22. Cathode brass. Plating same as 21.

23. Cathode brass. On removal from solution plate was very bright and metallic, but had split at one place and could be easily removed from the brass cathode. Thickness of plate 0.34 mm. at edge, 0.24 mm. at center.

24. Cathode brass. Smooth, uniform, white plate, readily buffed to mirror surface.

25. Cathode brass. Beautiful, bright, smooth plate, which began to separate from cathode at one corner.

26. Cathode brass. Very even, smooth deposit, having a good luster when polished.

27. Cathode brass. White plate, good luster when polished, somewhat rough on bottom, showing heavier deposit there, also small furrows from gas streaks.

28. Cathode brass. Splendid white deposit, but cracked a short distance in one place.

29. Cathode brass. Good white plate, but rough on bottom, showing heavier deposit there, also very small furrows from gas streaks.

30. Cathode brass. Burned, but not so badly as at 4.5 ampere current density.

31. Cathode brass. Plate burned along edges.

A number of the above platings were given a very severe bending test to study their adhesive qualities. In every case the plate stuck to the cathode after being bent backwards and forwards at an angle of nearly 180 degrees, in a manner equal to, if not better than, that of the best nickel plates with which we are familiar, subjected to a similar test. Even after the surface of the metal base had started to break, the cobalt plate still continued to cover the furrows and ridges formed.

FURTHER DATA OF PLATING EXPERIMENTS WITH COBALT SOLUTION I B.

Experiments at Russell Motor Car Company Plating Plant.

Solution: 5 lb. (2.3 kg.) salts; 6 gal. (27 liters) water; Sp. Gr., 1.050 — neutral.

Ref. No. of Experiment	Current Density		Electromotive Force, Volts	Electrode Distance, cm.	Cathode Area, Sq. cm.	Duration of Plating.		Anode Area, Sq. cm.
	Amp. per Sq. dm.	Amp. per Sq. ft.				Hr.	Min.	
32.	8.6	80.0	3.75	12.5	94	0	½	175
33.	3.4	31.6	3.25	12.5	281	0	40	350
34.	2.3	21.4	1.25	12.5	94	0	5	175
35.	4.3	40.0	2.0	12.5	94	0	5	562
36.	3.9	36.3	2.5	12.5	94	0	5	562
37.	3.3	30.7	3.0	12.5	62	0	30	175
38.	3.5	32.6	2.75	12.5	225	0	15	562
39.	3.3	30.7	3.0	12.5	94	0	50	175
40.	3.0	27.9	2.5	12.5	94	1	0	175
41.	3.0	27.9	2.5	12.5	75	0	15	175
42.	2.3	21.4	2.0	12.5	25	0	5	87.5
43.	3.0	27.9	2.5	12.5	75	0	15	175
44.	1.6	14.9	1.5	12.5	250	0	15	262
45.	1.0	9.7	1.5	12.5	250	0	5	262

32. Cathode steel. Blackened in 30 seconds.

33. Cathode steel. Poor plate, buffed easily, but blisters appeared, long and narrow in form, small pinholes on some portions. Slightly burned on lower ends.

34. Cathode brass hub-cap. Deposit slow, spotted, streaked, very dark.

35. Cathode brass hub-cap. Deposition rapid. Plate spotted, not uniform. Cathode not covered at end of run.

36. Cathode brass hub-cap. Plate same as 35.

37. Cathode steel. Good, firmly adherent plate. Very hard and smooth. Color similar to nickel before buffing. Colored easily and to good finish of slightly bluish tone.

38. Cathode steel. Did not cover; streaked, very hard brittle plate.

39. Cathode brass. Good color. Porous spots in casting, refused to cover at edges. Indented portions of cathode not coated. Spot beneath slinging wire bare.

40. Cathode brass. Struck the piece with nickel for 30 seconds. Cobalt deposit began readily and uniformly. Color darkened quickly, imperfect in spots, rough and streaked.

41. Cathode steel. Deeper portions of piece were not covered.

42. Cathode steel. Plate scaled, chipped. Deeper portions not covered.

43. Cathode steel. Solution slightly alkaline. Plate peeled badly. Several tests were made with similar results.

44. Cathode steel. Solution slightly acid. Plate very dark, otherwise a good plate, buffed easily, did not cut through.

45. Cathode steel. Plate very dark, buffed to good finish.

Data of Plating Experiments, Solution I B—Continued.

Ref. No. of Experiment	Current Density		Electromotive Force, Volts	Electrode Distance, cm.	Cathode Area, Sq. cm.	Duration of Plating.		Anode Area, Sq. cm.
	Amp. per Sq. dm.	Amp. per Sq. ft.				Hr.	Min.	
46.	2.3	21.4	1.5	12.5	225	1	0	262
47.	3.0	27.9	2.0	12.5	281	0	30	350
48.	3.0	27.9	2.0	12.5	250	0	30	350
49.								
50.	2.1	19.5	1.75	12.5	225	0	25	262
51.	3.9	36.3	2.0	20.0	75	0	5	175
52.	2.8	26.1	2.0	12.5	175	24	0	562
53.	3.7	34.4	2.25	12.5	113	2	0	350
54.	4.0	37.4	2.25	12.5	150	0	10	350
55.	3.7	34.4	2.0	12.5	75	0	15	175

46. Cathode steel. Surface covered instantly and in good condition. Gas liberated more freely than heretofore, but no indication of pinholes or streaks. Color very dark, resembling burnt nickel deposit. When dried it had a velvety appearance. Soft to the touch, buffed easily on soft wheel.

47. Cathode brass. Plate very dark. Surface covered with minute blisters or pits, which disappeared when buffed. Surface covered quickly and completely. Color satisfactory after buffing.

48. Cathode steel. Very dark, buffed easily and to good finish. Very hard plate, superior to 1 hour nickel from Prometheus.

49. Tests made during the following ten days resulted in similar plates, 6 lb. (2.7 kg.) cobalt salts were then added to the bath. Sp. Gr. 12° Bé. No further additions were made—bath very slightly acid. After ageing treatment the solution was practically neutral.

50. Cathode steel. Surface covered well, gas not as free as formerly, deposit marred by circular mark entire length and breadth of cathode. Color darker than nickel, hard and fine grained.

51. Cathode brass. Surface covered splendidly and color very good; withstood very hard buffing, but required only light treatment to finish. Very satisfactory results. Electrolyzed solution for 32 consecutive hours with an average current of 10 amperes at 2 volts—90 sq. in. anode surface. Added 24 drops liquid ammonia. Temperature 70 degrees F.; Sp. Gr. 1.085. Anode coated with brownish red film when at rest. Salts creep to hooks and remain moist. Solution neutral. Slight sediment at bottom of tank.

52. Cathode steel. Smooth, hard, adherent plate. No evidence of cracks or burning. Thickness approximately 1/32 inch (0.75 mm.).

53. Cathode steel tube. Smooth, white, hard plate. Drew the tube down from 1 in. (2.5 cm.) diameter to ⅝ in. (1.5 cm.) with no damage to deposit.

54. Cathode brass. Equal portions were nickel and cobalt plated for 1 hour. The two coatings were then buffed with same stroke. Repeated trials cut the nickel through before the cobalt. In no case did the cobalt expose the brass. Very convincing test.

55. Cathode brass. Plate of good color, buffed easily to splendid finish; bending, hammering, twisting did not crack or loosen plate.

Data of Plating Experiments, Solution I B—Continued.

Ref. No. of Experiment	Current Density		Electromotive Force, Volts	Electrode Distance, cm.	Cathode Area, Sq. cm.	Duration of Plating.		Anode Area, Sq. cm.
	Amp. per Sq. dm.	Amp. per Sq. ft.				Hr.	Min.	
56.	4.2	39.1	3.5	20.0	450	1	0	562
57.	4.5	41.8	4.0	20.0	450	1	0	562
58.	5.2	48.4	4.5	20.0	450	1	0	562
59.	5.2	48.4	4.5	20.0	75	1	0	87.5

56. Cathode sheet steel. The cathode consisted of six pieces steel hooked to wire frame. Plate good color, smooth, hard; did not crack when bent or twisted. Buffed to good finish.

57. Cathode steel. Deposit began with current density of 30 amp. per sq. ft. and gradually increased to 42. After 10 minute run with this current density, plate began to show signs of darkening. This, however, was not considered serious until expiration of 20 minutes. Entire surface finished easily on soft buff. While the plate was not a good specimen from a commercial view point, the remarkable efficiency of the bath was clearly demonstrated.

58. Same steel cathode as last test, arranged differently in frame. Plate gray but not burned; adherent, hard, smooth; did not break when bent; buffed easily to good finish.

59. This cast iron cathode was a piece of stove casting. Plate on one side only, and of splendid color over entire surface. The backgrounds being equally as white as average nickel plate. When buffed the piece could not be distinguished from nickel-plated piece.

Current densities as high as 6.3 amperes per square decimeter were employed in several further tests, but the results were not such as to merit recording. The solution at this time was proving very efficient in every detail.

NOTE:—To transform amperes per square decimeter to amperes per square foot, multiply by 9.3.

AGEING TEST OF SOLUTION I B.

	Grams Cobalt per 100 cc. Solution	Acidity of Solution
Solution at end of above series of experiments, August 26, 1914, after 80 hours plating as shown	2.54	Neutral
Same after 95 hours plating.....	2.58	"
Same after 110 hours plating.....	2.52	"
Same after 125 hours plating.....	2.55	"
Solution slightly diluted to original volume to make up for evaporation.		
Same after 140 hours plating.....	2.58	"
Same after 155 hours plating.....	2.60	"
Same after 170 hours plating.....	2.62	"

The last 90 hours plating with this solution were performed at a current density of 3.0 to 3.5 amperes per square decimeter. The cathode area was 34.0 square centimeters.

This solution is neutral to litmus paper, but very slightly alkaline, as shown by titration with 0.1 *N*. HCl and litmus indicator. The solution is remaining absolutely constant and the cobalt anode is dissolving satisfactorily.

CURRENT EFFICIENCY TEST SOLUTION I B.

RUN I.

Current density (approximate)	1.0 A. per sq. dec.
Cathode brass, asphaltum on back, area	29.2 sq. cm.
Time of run	1 hr. 0 min.
Average current through bath	0.300 A.
Theoretical weight of cobalt deposited	0.331 grams
Weight of cathode before plating	55.213 "
Weight of cathode after plating	55.536 "
Cobalt deposited	0.323 "

Current efficiency ..... $\frac{0.323}{0.331} = 0.977 = 97.7$ percent

RUN II.

Current density (approximate)	1.0 A. per sq. dec.
Cathode brass, polished both sides	47.4 sq. cm.
Time of run	1 hr. 0 min.
Average current through bath	0.475 A.
Theoretical weight of cobalt deposited	0.523 grams
Weight of cathode before plating	54.7641 "
Weight of cathode after plating	55.2774 "
Cobalt deposited	0.5133 "

Current efficiency ..... $\frac{0.513}{0.523} = 0.982 = 98.2$ percent

RUN III.

Current density (approximate)	3.0 A. per sq. dec.
Cathode brass, area	29.5 sq. cm.
Time of run	1 hr. 0 min.
Average current through bath	0.907 A.
Theoretical weight of cobalt deposited	0.996 grams
Weight of cathode before plating	69.279 "
Weight of cathode after plating	70.190 "
Cobalt deposited	0.911 "

Current efficiency ..... $\frac{0.911}{0.996} = 0.915 = 91.5$ percent

RUN IV.

Current density (approximate)	3.0 A. per sq. dec.
Cathode brass, polished on both sides	20.0 sq. cm.
Time of run	1 hr. 0 min.
Average current through bath	0.599 A.
Theoretical weight of cobalt deposited	0.659 grams
Weight of cathode before plating	19.3182 "
Weight of cathode after plating	19.9134 "
Cobalt deposited	0.5952 "

Current efficiency ..... $\frac{0.595}{0.659} = 0.903 = 90.3$ percent

RUN V.

Current density (approximate)	3.0 A. per sq. dec.
Cathode brass, polished on both sides, area	20.0 sq. cm.
Time of run	1 hr. 0 min.
Average current through bath	0.598 A.
Theoretical weight of cobalt deposited	0.659 grams
Weight of cathode before plating	20.2194 "
Weight of cathode after plating	20.8100 "
Cobalt deposited	0.5906 "

Current efficiency ..... $\frac{0.591}{0.659} = 0.897 = 89.7$ percent

The data of the plating experiments for solution I B show this solution to be remarkable for the extremely high current densities at which satisfactory plates may be obtained. We find no record of nickel plating being accomplished, except under special conditions such as with rotating cathodes, at anything like the same speed.

It is fairly well recognized that any improvement in the chemical composition of solutions for nickel plating, in order that a faster rate of deposition may be brought about, would have to be based upon a higher concentration of the nickel in the solution.

The inventors of "Prometheus," "Persels" and other salts for concentrated nickel solutions, no doubt had this in mind. These new baths are of comparatively recent invention, and there is considerable diversity of opinion as to their merits.

The practical plater knows that he can carry in his plating bath 12 oz. of double nickel-ammonium salt per gallon of water (80 g. per liter) in the summer and about 9 oz. of the same salt per gallon (60 g. per liter) in winter without danger of frequent crystallization. This first solution contains approximately 1.5 percent metallic nickel. On the other hand, using the Prometheus salts as bought on the market, as much as 2 lb. may be dissolved to the gallon of water (200 g. per liter) without danger of crystallization in the summer. Since this Prometheus salt contains about 28 percent of $NiSO_4$, this bath will contain approximately 2.6 percent of metallic nickel in solution. This tremendously increased metal content of the latter bath accounts for the greater speed at which plating is possible with it.

Comparing the cobalt solution I B with this, we note that it contains 200 grams of $CoSO_4.(NH_4)_2SO_4.6H_2O$ to the liter, so that its concentration in metallic cobalt is approximately 3.0

percent. We would, therefore, expect this solution to be a very rapid plating one, faster than the other, as we find it to be, but the figures do not account for the great difference between the solutions. It also has the advantage of being free from magnesium sulphate, boric acid and the like, which are very considerable and necessary constituents of all the concentrated fast-plating nickel solutions. Moreover, we find with all solutions of this type that the cobalt bath is much more rapid plating than the nickel bath, taking them at the same concentration. Experiments conducted under conditions of present plating practice, demonstrate that this solution I B, was capable of plating cobalt satisfactorily at several times the speed that the Prometheus salt was capable of plating nickel. (See page 92.) This comparison was for the best condition for each that was known either to the practical plater in charge of the plating establishment in question, or to us, as a result of these experiments.

CONCLUSIONS.

I. Cobalt plates from these cobalt-ammonium sulphate solutions, on brass and iron, are firm, adherent, hard and uniform, and may readily be buffed to a satisfactorily finished surface. They take a very high polish, with a beautiful lustre, which although brilliantly white, possesses a slightly bluish cast.

II. The specific electrical conductivity of these cobalt-ammonium sulphate solutions is very much higher than that of the corresponding nickel solutions.

III. All of these cobalt plates within the current density ranges described as satisfactory, are as smooth, adhesive and generally satisfactory as the best nickel plates.

IV. Solution I B, which is a nearly saturated solution of $CoSO_4.(NH_4)_2SO_4$, containing 200 grams of

$$CoSO_4.(NH_4)_2SO_4.6H_2O$$

to the liter of water, yields satisfactory cobalt deposits at all current densities up to 4 amperes per square decimeter (37.2 amperes per square foot.) This very rapid plating was performed in a manner similar to that of common plating practice.

V. There is no nickel bath operating in the manner of the usual commercial plating procedure at anything like as high

a current density as cobalt bath I B. More specifically, the allowable current density with which an adherent, firm, smooth, white, hard plate may be obtained with solution I B, without sign of pitting or peeling, and yet which may be readily and satisfactorily finished, is four times that for which the same results may be obtained with the fastest commercial nickel solutions.

VI. Bath I B may be used for plating on the usual surface, including brass, iron and steel. No preliminary coating of copper is necessary when plating with these baths on iron and steel.

VII. Solution I B may be used with a large proportion of rolled anodes without becoming acid or depleted in metal.

VIII. Solution I B does not change appreciably in cobalt content or in acidity when used over long periods of time at the high recommended current density.

IX. The current efficiency of solution I B is extremely high at a current density of 1 ampere per square decimeter. The mean of our measurements, agreeing very well among themselves, gave a value of 98.0 percent. The current efficiency of solution I B is as high at 3 amperes per square decimeter as is common for the best nickel solutions used in nickel plating practice at very much lower current densities. The average of three closely agreeing current efficiency measurements with solution I B, at 3 amperes per square decimeter was 90.5 percent.

XII. Solution I B, when operated slightly alkaline yields plates which are grayish in color, which peel, pit and show blisters. This solution, when operated acid yields plates which, while fairly adherent, firm and smooth, are dark and freakish.

This bath should be run neutral, for these plates are adherent, firm, smooth, white, hard, yet easily buffed to an excellent finish.

XIII. Solution I B requires very little, if any, ageing to put it in condition, but yields satisfactory plates almost from the start.

XIV. The "throwing" power of solution I B is remarkably satisfactory.

XV. The anodes in solution I B are remarkably free from a coating, such as characterizes nickel anodes.

Solution I B shows so many superior qualities that it seems highly worth while to develop it further, and particularly to study it under exact commercial conditions. This work is reported in a later paragraph under "Commercial Tests with Solution I B," see page 106 *et seq.*

BATH XIII B.

Cobalt sulphate, $CoSO_4$	312.5 grams
Sodium chloride, NaCl	19.6 grams
Boric acid	nearly to saturation
Water	1000 c.c.
Total bath, approximately	1½ liters

This solution is substantially saturated in cobalt sulphate in the presence of the other components. Its specific gravity at 15° C. is approximately 1.24.

DATA OF PLATING EXPERIMENTS SOLUTION XIII B.

Reference No. of Experiments	Current Density		Electromotive Force, Volts	Electrode Distance, cm.	Cathode Area, Sq. cm.	Duration of Plating,	
	Amp. per Sq. dm.	Amp. per Sq. ft.				Hr.	Min.
60.	0.50	4.7	1.02	10	33.6	3	0
61.	0.75	7.0	1.23	10	32.6	1	30
62.	1.0	9.3	1.53	10	34.0	1	0
63.	1.25	11.6	1.75	10	34.0	1	0
64.	1.50	13.9	1.25	10	32.0	1	0
65.	5.46	50.8	5.5	10	34.8	0	30
66.	6.0	56.8	....	10	32.7	0	10
67.	6.15	57.2	6.0	10	32.7	0	15
68.	8.0	74.4	4.83	10	17.6	0	12
69.	8.0	74.4	6.0	10	20.0	0	10

60. Cathode brass. Uniform, rough, dark plate. Impossible to polish without grinding.

61. Cathode brass. Smooth, uniform, gray plate, which buffed to satisfactory finish with difficulty.

62. Cathode brass. Uniform, dark gray deposit, difficult to buff.

63. Cathode brass. Plate same as 62.

64. Cathode brass. Uniform, smooth gray plate, which buffed somewhat more readily than preceding plates with this solution.

65. Cathode brass. Good, smooth, white deposit, which buffed readily to mirror surface.

66. Cathode brass. Good, smooth, white deposit, buffed readily to mirror surface.

67. Cathode brass. Plate same as 66. Solution had been subjected to severe ageing test, as described below.

68. Cathode brass. Plate same as 67.

69. Cathode iron. Good, smooth, white deposit, which buffed readily to mirror surface. This plate was given a severe bending test, being doubled on itself backwards and forwards to an angle of 180 degrees. The metal furrowed and split on surface and end, but plate clung absolutely.

Data of Plating Experiments, Solution XIII B—Continued.

Reference No. of Experiments	Current Density		Electromotive Force, Volts	Electrode Distance, cm.	Cathode Area, Sq. cm.	Duration of Plating,	
	Amp. per Sq. dm.	Amp. per Sq. ft.				Hr.	Min.
70.	8.0	74.4	6.0	10	20.0	0	10
71.	8.8	81.8	6.5	10	22.5	0	12
72.	8.88	82.6	5.90	10	20.0	0	15
73.	9.77	90.8	6.5	10	22.5	0	12
74.	10.7	99.9	6.3	10	1.81	0	20
75.	10.0	93.0	....	10	17.6	0	5
76.	14.6	136.0	6.5	10	14.7	0	5
77.	16.5	154.0	5.7	10	10.0	0	5
78.	17.5	163.0	6.85	10	10.6	0	5
79.	5.35	49.8	6.0	10	32.8	15	15
80.	16.5	154.0	5.5	10	10.0	17	30
81.	5.26	48.9	6.0	10	18.9	67	0
82.	9.0	83.8	5.5	10	18.3	0	5
83.	3.77	35.1	5.5	10	60.1	0	10
84.	3.83	35.6	5.5	10	60.1	0	20

70. Cathode iron. Plate same as 69.

71. Cathode iron. Good, smooth, white deposit, which buffed readily to mirror surface.

72. Cathode brass. Solution severely aged. Good, smooth, white deposit, which buffed readily to mirror surface.

73. Cathode iron. Plate same as 72.

74. Cathode iron. Plate same as 73.

75. Cathode brass. Plate same as 74.

76. Cathode brass. Plate same as 75. This is the best deposit obtained with this solution to date, although all plates at current densities from 6 amperes per sq. dm. up were good.

77. Cathode brass. Good, smooth, white deposit, readily buffed to mirror surface. Excellent plate.

78. Cathode brass. Plate same as 77.

79. Cathode heavy sheet brass. Firm, adherent, massive plate, showing no tendency to split or curl. Smooth in center, with nodules at edges. Weight approximately 37 grams, thickness approximately 1 mm. The area of the effective cathode increased from 32.8 sq. cm. at the start, to approximately 40.0 sq. cm. at the end of the run. This latter figure is not sufficiently accurate to admit of exact computation, but the figures show in a general way that the current efficiency was very high.

80. Cathode brass. Firm, adherent, massive plate, showing no tendency to split or curl. Weight about 30 grams.

81. Cathode circular brass plate. Firm, adherent, massive plate, showing no tendency to split or curl; about 5 mm. thick.

82. Brass cathodes with grooves, depth 1.62 mm. to 7.0 mm. to study "throwing" property of this solution. Good, smooth, uniform, white deposit. All grooves satisfactorily covered, and satisfactorily buffed to mirror finish.

83. Cathode brass block. Plate same as 82.

84. Brass block cathode, with grooves faced toward anode, but entire block, back as well as grooves, satisfactorily covered to admit of severe and satisfactory buffing after only 10 minutes' plating. Plate same as 83.

FURTHER DATA OF PLATING EXPERIMENTS WITH COBALT SOLUTION

XIII B.

Experiments at Russell Motor Car Company Plating Plant.

Solution: Water, 4¾ gal. (21.6 liters); Boric acid, 3 lb. (1.35 kg.); NaCl, 15½ oz. (440 g.); Cobalt, sulphate crystals, 26 lb. 10½ oz. (12.2 kg.); Strongly acid; Sp. Gr., 28.5° Bé.; Temp., 64° F.

Reference No. of Experiments	Current Density		Electromotive Force, Volts	Electrode Distance, cm.	Cathode Area, Sq. cm.	Duration of Plating,	
	Amp. per Sq. dm.	Amp. per Sq. ft.				Hr.	Min.
85.	6.5	60.5	4.25	12.5	75	0	5
86.	4.4	40.9	3.5	12.5	175	1	0
87.	3.2	29.8	3.5	12.5	265	1	0
88.	3.5	32.6	5.0	12.5	438	0	30
89.	9.0	83.7	4.0	12.5	75	0	5
90.	12.0	112.0	6.0	12.5	75	0	5
91.	13.1	122.0	4.5	6.25	25	0	2
92.	21.4	198.0	6.0	12.5	25	0	2
93.	20.0	186.0	6.5	12.5	25	0	2
94.	6.9	64.2	4.5	12.5	56	0	15
95.	8.3	77.2	4.0	12.5	59	0	10
96.	4.2	39.1	3.5	12.5	175	0	50
97.	8.6	80.0	9.0	12.5	103	0	1

85. Brass cathode. Smooth, hard, firm plate, very adherent; stood bending test and twisting. Buffed on 12-inch cotton buff wheel at 3,600 r. p. m., with pressure approximately same as for heavy nickel plate. No evidence of cutting through; splendid results.

86. Steel cathode. Mottled burnt deposit, impossible to buff or polish to a satisfactory surface. Solution full of floating particles of boric acid.

87. Brass cathode. Filtered solution. Mottled, cloudy plate at edges, center quite brilliant, but difficult to color. Poor plate.

88. Cathode brass hub-cap. Very heavy, dirty gray plate, flaked on sides, burnt on edges, rough and impossible to color. Inside well covered (2½ inches deep).

89. Cathode brass. Plate gray, streaked.

90. Cathode brass. Plate whiter, better than last test.

91. Cathode brass. White, tough plate at center, edges badly burnt.

92. Cathode copper. Excellent deposit of good thickness, corners cracked only slightly. Deposit could be felt with finger nail; buffed to good color. Did not crack when bent double.

93. Cathode copper. Plate same as 92.

94. Cathode copper. Smooth, hard, white, adherent plate. Buffed to good finish.

95. Cathode corrugated steel. Best plate thus far. Buffed to mirror finish over entire surface. Deepest grooves in good condition.

96. Cathode thick steel. Plate appeared satisfactory when removed from bath, but scaled at center when dipped in hot water.

97. Cathode brass. Smooth, uniform, white plate; withstood hard buffing. Colored easily to mirror finish.

Data of Plating Experiments, Solution XIII B—Continued.

Reference No. of Experiments	Current Density		Electromotive Force, Volts	Electrode Distance, cm.	Cathode Area, Sq. cm.	Duration of Plating,	
	Amp. per Sq. dm.	Amp. per Sq. ft.				Hr.	Min.
98.	8.6	80.0	8.0	12.5	281	0	1
99.	19.4	181.0	8.0	12.5	50	0	2
100.	19.4	181.0	8.0	12.5	50	0	1
101.	9.7	90.3	6.0	12.5	50	0	5
102.	10.7	99.5	3.0	12.5	50	0	15
103.	16.8	156.0	6.0	12.5	113	0	1
104.	17.1	159.0	6.5	12.5	75	0	1
105.	19.4	181.0	6.5	12.5	450	0	1
106.	26.4	246.0	6.5	12.5	15.6	0	1
107.	16.9	157.0	6.5	12.5	75	0	5
108.	16.8	156.0	6.5	12.5	187	0	5
109.	16.8	156.0	6.5	12.5	208	0	5
110.	17.0	158.0	6.0	12.5	62.5	0	2
111.	16.8	156.0	6.5	12.5	93.7	0	5
112.	16.3	152.0	6.5	12.5	281	0	3

98. Cathode brass hub-cap. Smooth, white plate, buffed to excellent finish. No evidence of a defect.

99. Cathode perforated brass. Plate showed beautiful results; high and low spots perfect.

100. Cathode same as 99. Cleaned the piece just plated and plated on the first deposit without stripping. No indication of trouble from this source.

101. Cathode same as 100. Splendid plate, colored by rubbing with flannel cloth, afterwards stood severe buffing test.

102. Cathode same as 101. Dull, muddy color when removed from bath; buffed readily to good luster. Background not as white as when higher voltage was used.

103. Cathode cast iron. Burnished the piece with 400 lb. of steel balls for 15 minutes; good finish. No evidence of wearing through deposit. Placed the casting in acidulated water (15 to 1) for 36 hours, wiped dry. No evidence of defective coating, casting remained in good condition.

104. Cathode embossed brass. Buffed on 10-inch wheel at 3,600 r. p. m.; excellent finish. Did not cut through letters or raised parts.

105. Cathode 6 embossed brass pieces. Excellent plate.

106. Cathode brass. Splendid plate; hard yet pliable. Plated 200 of these pieces in same manner, in one dozen lots.

107. Cathode polished lead. Adherent plate, hard, smooth and good color; buffed readily. Did not break when bent. Cut lead in pieces without scaling deposit.

108. Cathode britannia metal. Very satisfactory plate, adherent and white.

109. Cathode steel skate blade. Not as white as desired, but otherwise very good plate.

110. Cathode German silver. Excellent plate.

111. Cathode tin. This deposit stood every conceivable abuse, and was easily colored on small buff.

112. Cathode brass hub-cap. Buffed to a beautiful finish. Required very severe buffing on wheel revolving at 1,500 r. p. m., to cut through; apparently equal to a 1 hour nickel deposit.

Data of Plating Experiments, Solution XIII B—Continued.

Reference No. of Experiments	Current Density		Electromotive Force, Volts	Electrode Distance, cm.	Cathode Area, Sq. cm.	Duration of Plating,	
	Amp. per Sq. dm.	Amp. per Sq. ft.				Hr.	Min.
113.	17.0	158.0	6.5	12.5	62.5	0	1
114.	17.0	158.0	6.5	12.5	375	0	1
115.	16.8	156.0	6.0	12.5	113	0	15
116.	11.6	108.0	6.0	12.5	75	15	15
117.	21.1	196.0	6.5	12.5	25	0	5
118.	16.8	156.0	6.5	6.25	75	0	5
119.	20.0	186.0	6.5	12.5	25	0	10

113. Cathode brass. Plated 100 pieces, and buffed them ready for stock in 1 hour.

114. Same as 113.

115. Cathode steel tube. Drew tube from 1 to ¾ in. (2.5-1.9 cm.), buffed same and found perfect, then drew tube to ⅝ in. (1.6 cm.), buffed again and still perfect.

116. Cathode oxidized, silver-faced britannia metal. Anode surface 87 sq. cm. The die was merely washed with alcohol, rinsed in water and placed in cobalt bath. A current of 15 amperes was passed through the bath for 10 minutes, while the cathode was kept constantly moving. Current then reduced to 9 amperes and cathode closely watched during the following hour. Bath switched to battery circuit and allowed to remain undisturbed during the night. Resulting deposit was quite smooth at center, edges rough but solid; face of die in fine condition. The finest lines perfect. The deposit did not curl or lift from the master-die during run. Deposit about 3/32 in. (0.24 cm.). Extraordinary results for die work.

117. Cathode brass, 1/32 in. (0.08 cm.) thick. Splendid plate; beautiful color after buffing.

118. Cathode brass. Firm, tough, adherent plate, white in color; began to darken at edges; oiled off edges with emery, then buffed entire surface to splendid finish.

119. Cathode brass. Adherent, white, smooth plate; buffed very easily to good finish.

AGEING TEST OF SOLUTION XIII B.

	Grams Cobalt per 100 cc Solution	Acidity of Solution
Solution after plating as shown in above table to October 6, 1914, approximately 2 hours	8.55	Strongly acid to litmus
Solution after further run 15 hours, 15 minutes, depositing approximately 37.0 grams at current density 5.35 amperes per square decimeter, October 7th	8.40	Strongly acid to litmus
Solution after 17.5 hours further plating depositing about 30 grams at current density of 16.5 amperes per square decimeter, October 8th	8.20	Strongly acid to litmus

After all the above use, a good, smooth, white plate was obtained at 15.4 amperes per square decimeter in 5 minutes, which buffed readily to mirror surface.

	Grams Cobalt per 100 cc. Solutfon	Acidity of Solution
Solution after 15 hours further plating at 11 amperes per square decimeter, depositing approximately 40 grams, October 9th	8.30	Strongly acid to litmus
Solution after 16 hours further plating at 5.0 amperes per square decimeter, October, 10th	7.95	Strongly acid to litmus
Solution after 67 hours further plating at 5.26 amperes per square decimeter, October 13th	7.59	Strongly acid to litmus

After all the above use, a good, smooth, white plate was obtained at 16.5 amperes per square decimeter in 5 minutes, which buffed readily to mirror surface.

These ageing tests were run at very severe anode current densities, so that the solution behaved remarkably well under the circumstances.

CURRENT EFFICIENCY TEST SOLUTION XIII B.

RUN I.

Current density (approximate) ..... 1.2 A. per sq. dec.
Cathode brass, polished both sides, area ..... 35.0 sq. cm.
Time of run ..... 1 hr. 0 min.
Average current through bath ..... 0.435 A.
Theoretical weight of cobalt deposited ..... 0.478 grams
Weight of cathode before plating ..... 30.9971 "
Weight of cathode after plating ..... 31.4783 "
Cobalt deposited ..... 0.4812 "

Current efficiency ..... $\frac{0.481}{0.478} = 1.0 = 100.0$ percent

RUN II.

Current density (approximate) ..... 1.0 A. per sq. dec.
Cathode brass, polished both sides, area ..... 32.4 sq. cm.
Time of run ..... 1 hr. 0 min.
Average current through bath ..... 0.324 A.
Theoretical weight of cobalt deposited ..... 0.356 grams
Weight of cathode before plating ..... 23.2262 "
Weight of cathode after plating ..... 23.5825 "
Cobalt deposited ..... 0.3563 "

Current efficiency ..... $\frac{0.356}{0.356} = 1.0 = 100.0$ percent

RUN III.

Current density (approximate)	5.0 A. per sq. dec.
Cathode brass, polished both sides, area	18.2 sq. cm.
Time of run	1 hr. 0 min.
Average current through bath	0.922 A.
Theoretical weight of cobalt deposited	1.012 grams
Weight of cathode before plating	27.9628 "
Weight of cathode after plating	28.9726 "
Cobalt deposited	1.009 "
Current efficiency	$\frac{1.009}{1.012} = 0.996 = 99.6$ percent

CONCLUSIONS.

I. Solution XIII B is the most completely satisfactory solution, for a great variety of purposes, which we have found. We know of no solution, plating with nickel, which begins to compare with solution XIII B for the range of work which it will do, and for the extreme high current densities at which it will operate. It is possible to get a plate in three minutes or less, with solution XIII B, which will stand all the usual physical commercial tests, and which will buff as satisfactorily as a plate which has taken one hour from the usual nickel plating baths.

II. Cobalt plates from this simple cobalt sulphate solution in the presence of sodium chloride and boric acid (bath XIII B) on brass and iron, are firm, adherent, hard and uniform, and may readily be buffed to a satisfactorily finished surface. They take a very high polish, with a beautiful lustre, which, although brilliantly white, possesses a slightly bluish cast.

III. The specific electrical conductivity of solution XIII B is much higher than that of the corresponding nickel solution.

IV. Solution XIII B does not yield the best cobalt plate at low current densities, that is, in the neighborhood of 0.50 to 1.0 ampere per square decimeter, which is a common range for nickel plating work. Solution XIII B begins to plate most satisfactorily at a current density in the neighborhood of 3.5 amperes per square decimeter, and continues to give satisfactory plates at all current densities up to 26.4 amperes per square decimeter. This is equivalent to a current density of over 240 amperes per square foot, and even at this speed, the limit of the solution has not yet been reached.

V. All of these cobalt plates within the wide current density range described as satisfactory for solution XIII B, are as

smooth, adhesive and generally satisfactory as the best nickel plates.

VI. Solution XIII B does not change appreciably in cobalt content or in acidity when used over long periods of time at current densities as high as 1 ampere per square decimeter. It only showed a very gradual diminution in cobalt content under the most severe conditions of the ageing test described above. We know of no other cobalt solution and of no nickel solution which would stand up under the conditions of this ageing test.

VII. There is no nickel bath of which we are aware operating in the manner of the usual commercial plating procedure at anything like as high current density as bath XIII B.

VIII. Solution XIII B may be used for plating on brass, iron and steel, for which cathodes the above conclusions apply.

IX. Solution XIII B may be used to deposit a heavy cobalt plate. These plates may apparently be deposited to any desired thickness, and they are firm, adherent, massive, of extreme hardness and show no tendency to curl or split.

X. Heavy plates may be obtained from solution XIII B to much better advantage than solution XV,[15] which has been patented for the purpose with nickel, that is, heavy deposits may be obtained from solution XIII B at current densities of 5 or 6 amperes per square decimeter whereas solution XV must be operated at low current densities in the neighborhood of 0.30 amperes per square decimeter. If a current density of above 6 amperes per square decimeter is used with solution XIII B for heavy deposits, under the conditions in dimension of our baths, it was found that trees were formed on the cathode.

XI. Our experiments show that solution XIII B "throws" very satisfactorily.

XII. Among the satisfactory properties of this remarkable solution should be mentioned an extremely high current efficiency, which we found at 1.0 and 5.0 amperes per square decimeter to be almost 100 percent.

XIII. Solution XIII C, which is the nickel analogue of solution XIII B, yielded satisfactory plates up to about 5 amperes per square decimeter, but showed splitting at current densities

[15] Cobalt ethyl sulphate 100 g.; Sodium sulphate 10 g.; Ammonium chloride 5 g.; Water 1,000 cc. G. Langbein & Co., D. R. P. 134736, Sept. 18, 1902.

greater than that. Nickel solution XIII C does not possess the remarkable qualities of its cobalt analogue XIII B, although in many respects it is an improvement on standard nickel solutions.

XIV. Solution XIII B requires very little ageing; it operates satisfactorily almost from the start.

XV. Solution XIII B is so remarkable in its properties that it was thought highly worth while to develop it further under commercial conditions. See commercial tests, page 110 *et seq.*

COMMERCIAL TESTS WITH SOLUTION I B.

Verification of Plating Results on Commercial Scale.

The results with solution I B (and later with solution XIII B) were thought by the authors to be unusual and of sufficient importance to warrant verification and further development under standard commercial conditions. We therefore arranged with the Russell Motor Car Company of Toronto, Ontario, and particularly with Mr. W. S. Barrows, Foreman Electroplater, with the same company, to have a plating tank operated under standard commercial conditions at their plant, using solution I B and later solution XIII B.

Mr. Barrows has had some twenty years of experience with all sorts of electro-plating work, to which he has particularly devoted himself. He has considered these two solutions entirely from the point of view of commercial practicability and value.

The authors take great pleasure in expressing their thanks to the Russell Motor Car Company, and to Mr. W. S. Barrows, for their collaboration, and particularly to Mr. Barrows for the careful, vigorous and painstaking manner in which he has subjected the solutions and plates to the various tests that were required, to establish their commercial importance and value.

SOLUTION I B.

Salts identical with those used in this laboratory were sent by the authors to Mr. Barrows, with instructions for making up solution I B identical with that used by us and described on page 17.

Anodes: Cobalt anodes were cast at this laboratory of the size required by Mr. Barrows for his tank, and sent him for use in these experiments. They analyzed as follows:

Co	98.75
Ni	none
Fe	1.35
As	none
P	0.0067
S	0.052
C	0.061

The anodes used in a bath had a surface of approximately 1 square foot area (9.3 sq. dm.).

Tests: Mr. Barrows, in collaboration with the authors, tested solution I B for plating purposes, during the months of August and September, 1914. The plating was accomplished under standard commercial conditions on copper, brass, iron, steel, tin, German silver, lead and Britannia metal. Various articles, such as brass castings, sheet brass, steel stampings, skates, automobile hubs, etc., etc.—articles of very different shapes and sizes were plated under exactly the same general conditions as for nickel plating practice at the Russell Motor Car Company.

The tests were made in a still solution, that is without agitation of any kind, and the resulting plates were subjected to the most severe practical tests. This work was regarded by Mr. Barrows purely from the commercial viewpoint, and with this in mind he particularly tested and studied the following points—the color of plate, its uniformity and freedom from defects, the allowable speed of plating without pitting or burning, the maximum allowable current density, the solubility of the anodes, the required voltage, the "throwing" properties of the bath, that is, its ability to cover the deeper parts of the object in a satisfactory manner, the solubility of the salts, the hardness of the plate, the ease of "coloring" the plate on a buff, the efficiency of the plating solution, the time required for ageing the bath, the adhesiveness of the plate to the cathode under bending and hammering tests, the general cleanliness of the bath, the corrosion of the plate, besides many other special features.

In a letter to one of the authors, dated November 2d, Mr. Barrows gives a very complete report of his commercial tests of solution I B. This letter follows, and serves admirably to cover this portion of the work:

REPORT OF MR. BARROWS.

"After preparing a cobalt plating solution according to your formula for bath I B, and having used this bath daily during the past eight weeks, plating a great variety of copper, brass, iron, steel, tin, German silver, lead, and Britannia metal articles of different shapes and sizes under exactly the same conditions as met with in general nickel plating at the factory of the Russell Motor Car Company, West Toronto, and after regarding the characteristics of this particular solution absolutely from a commercial viewpoint, I can heartily confirm any statement you have made to me regarding this remarkable solution. This bath was equipped with cobalt anodes, 98.75 percent cobalt, which were sent to me from your laboratory."

"The runs made have varied from five minutes to 24 hours, and in each case the bath has proved wonderfully efficient."

"The cobalt plates obtained were smooth, white and fine grained, very adherent and uniform. In fact the surfaces of these deposits after several hours' run were so very smooth and uniform, that a 4-inch cotton buff colored them to a mirror finish quite easily. We use 14-inch and 16-inch buffs to color 3-hour deposits of nickel."

"To test the hardness of the cobalt as compared with nickel, with reference to either buffing or polishing with emery, we plated strips of brass, one-half the surface with cobalt and one-half with nickel, always giving the nickeled portion the thickest plate. Then buffing or polishing across the two deposits we found invariably that the nickel was removed from the brass before the cobalt, and in some cases in one-half the time."

"Though so hard and firm, these plates color beautifully with little effort, and require the use of much less buffing composition than comparatively thin plates of nickel. Automobile parts of irregular shape were plated from 10 to 20 minutes, and finished on a 6-inch buff operated at 3,000 R. P. M. without the silghtest evidence of a defect in the plating. To accomplish this with our fastest nickel baths would require at least 60 minutes of plating."

"As a protective coating for iron or steel surfaces, I am convinced that a comparatively thin plate of cobalt will prove

equally as effective as a thick plate of nickel from an ordinary double sulphate nickel bath, and the time and power required for the production of such plates is decidedly in favor of the cobalt."

"The deposits are also very adherent, no difficulty having been experienced in this respect, although tests were made repeatedly by bending, hammering and burnishing."

"One of the weak points of several so-called rapid nickel plating solutions which we have tried commercially, is their poor 'throwing' powers—*i.e.*, they do not deposit the nickel readily in the indentations or cavities of the cathode. The cobalt solution I B meets this requirement in a most efficient manner, the deposits on the distant portions of the cathode withstand the tests imposed in every case."

"Another most important feature of this solution, which should commend itself to every practical plater and manufacturer of plated wares, is the extremely high current density at which this solution may be employed without danger of pitting the plated surface. I have plated with this cobalt solution I B satisfactorily and under commercial conditions, at a current density of 42 amperes per square foot. This is 4.2 times the speed of our fastest commercial nickel solutions."

"As a further test we plated steel tubes of 1-inch diameter (2.5 cm.) for two hours, with a current density of 27 amp. per square foot, and then drew the tubes down to 0.625 inch diameter without injuring the deposit. Though extremely hard, the ductility of the deposited metal proved remarkable."

"All of our tests have been made in a still solution, without agitation of any kind, and the plates were subjected to the most severe treatment considered practical for high-grade metallic coatings on the various metals heretofore mentioned."

"We are also of the opinion that the anodes in the cobalt bath I B will remain free from coatings, such as characterize average anodes used in nickel baths, and that the cost of maintenance will be practically nothing compared to double sulphate nickel solutions."

"I can assure you that my experience thus far with these cobalt solutions has been intensely interesting, and I sincerely

believe that their use commercially would revolutionize the art of electro plating such wares as are now nickel plated."

"The simplicity of its composition, its self-sustaining qualities, the remarkable speed of deposition, together with the several points mentioned previously, should appeal to the commercial requirements of this progressive age."

COMMERCIAL TESTS WITH SOLUTION XIII B.

After the completion of the tests on solution I B by Mr. Barrows, salts identical with those used by the authors were sent to him, with instructions for preparing bath XIII B, identical with that described on page 98.

Anodes: Identical with those used for solution I B, see page 106.

Tests were made of this solution in the manner and from the same point of view as those for solution I B. (See page 107.)

In a letter to one of the authors, dated December 1st, Mr. Barrows gives a complete report of his commercial tests of solution XIII B. This letter follows:

REPORT OF MR. BARROWS.

"After thoroughly testing cobalt plating bath XIII B, made according to your formula, I take pleasure in submitting the following report."

"I found the bath very simple to prepare and at once began to operate the solution with high current densities. The results obtained were exceedingly gratifying. Evidently bath XIII B will require no prolonged ageing treatment, as splendid, white, hard, perfect deposits were obtained with extremely high current densities within three hours after bath was prepared."

"The experiments have been varied and the tests of plates severe and deliberate, the results have invariably been such as to cause me to regard cobalt bath XIII B the greatest achievement in modern electro-plating improvements."

"The operation of the bath is positively fascinating, the limit of speed for commercial plating is astonishing while the excellence of the plates produced is superior to those of nickel for many reasons."

"The efficiency of the freshly prepared solution, together with

the self-sustaining qualities of the bath are without a parallel in any plating solution of any kind I have ever used."

"Thin embossed brass stampings were plated in bath XIII B for only one minute, then given to a buffer who did not know the bath existed and who was accustomed to buffing 1¼-hour nickel deposits on these same stampings. This man buffed the cobalt plates upon a 10-inch cotton buff wheel revolving at 3,000 R. P. M. The finish was perfect with no edges exposed. These stampings have been plated in two dozen lots for one minute, and from a total of 500 stampings we have found but three stampings imperfect after buffing. Each stamping is formed to a spiral after finishing, without injury to the deposit. Grey iron castings with raised designs upon the surface were plated one minute in cobalt bath XIII B, then burnished with 400 lb. of ⅛-inch steel balls for ¼ hour without the slightest injury to the cobalt coating, as was proven by a 36-hour immersion in 15 ozs. of water acidulated with 1 oz. of sulphuric acid."

"While attempting to reach the limit of current densities which would be practical with this bath XIII B, I have plated brass automobile trimmings with a current density of 244 amperes per square foot. These pieces were plated in lots of 6, and a total of 100 were plated, buffed and ready for stock in 1 hour's time. No unusual preparation was made for the run and the work was performed by one man. Size of piece plated 1½ in. x 5 in.

"Automobile hub-caps were plated three minutes in cobalt bath XIII B and buffed to a beautiful lustre of deep rich bluish tone by use of a 7-inch cotton buff revolving at 1,200 R. P. M. The deposits were ample for severe treatment usually received by such articles. Comparative tests of these deposits were made as follows: Same style castings plated in double sulphate nickel solution one hour were suspended as anodes in a solution of equal parts muriatic acid and water, sheet lead cathodes were used and a current of 200 amperes at 10 volts passed through the bath. The nickel was removed from the castings in 30 seconds while 45 seconds' time was required to remove the cobalt plates."

The above mentioned plating tests were made with still solution, no form of agitation being employed. By aid of mechan-

ical agitators these current densities could be greatly exceeded with highly satisfactory results."

"These cobalt plates were very hard, white and adherent and colored easily with slight effort."

"Several plates were produced upon sharp steel surgical instruments, these instruments finished perfectly and owing to the hardness of the cobalt plate only a thin deposit was required to equal the best nickel deposits which we received as samples. Cobalt deposits should prove especially valuable for electroplating surgical instruments for this reason, non-adherent thick deposits being very dangerous for this class of work."

"Owing to the unusual mild weather in this locality during the past month, I have not concluded test with cobalt plates on highly tempered nickel-steel skate blades, but judging from appearances and various severe indoor tests we do not hesitate to report success in this direction. A three-minute deposit from bath XIII B resists corrosion equally as long as a one-hour nickel deposit, the finish is even superior to nickel, while every test employed during the process of manufacturing the nickel-plated article has proved equally ineffective with cobalt plates, therefore by reason of the effectiveness of thin cobalt deposits we believe cobalt plates should prove wonderfully efficient on skates, or any keen edged tool requiring a protective metallic coating."

"The runs made with bath XIII B have varied from one minute to 15½ hours, and in each case the results were remarkable. Electrotypes were reproduced $\frac{1}{16}$-inch thick. Electro-dies were faced with cobalt ⅛-inch thick, the electrotypes being graphite covered wax and lead moulds, while the dies were made on oxidized silver faced Britannia metal."

"The deposits from cobalt bath XIII B were very adherent and pliable, by proper regulation of the current beautiful white, hard, tough plates may be produced quickly on any conducting surface."

"The 'throwing' powers of cobalt bath XIII B make possible its employment for plating deeply indented or grooved articles such as reflectors, channel bars or articles with projecting portions."

"We also obtained the best plates with extremely high cur-

rent densities, although plates finished with 75 amperes per square foot were of good color and easily buffed. The production of excellent plates with a current density of 150 amperes proved particularly easy and densities in this neighborhood were employed for the greater portion of our tests."

"Cobalt bath XIII B will produce excellent hard, white, tough plates absolutely free from pits or blemish at a current density of 150 amperes per square foot and under ordinary commercial conditions. This is 15 times the speed of our fastest commercial nickel solution."

"Furthermore, the anode tops and hooks remain free from creeping salts. The solution retains its original clean appearance and the anodes dissolve satisfactorily, no slime or coating formed, brushing or cleaning anodes therefore will be unnecessary. The anodes used with this bath were 98.75 percent cobalt which were sent me from your laboratory. The bath at the commencement of our tests was strongly acid to litmus, and has remained unchanged throughout our experiments. The specific gravity of the solution when freshly prepared was 1.24 and is the same today."

"The rich deep bluish-white tone of the cobalt plates upon polished brass surfaces is particularly noteworthy. This feature should assist greatly in making cobalt deposits very popular for brass fixtures, trimmings and plumbers' supplies."

"My experience with cobalt bath XIII B is by no means at an end. I intend to continue its use until present supplies are exhausted and then equip a larger bath if supplies are obtainable. As a commercial proposition I am satisfied it is wonderfully efficient and economical."

"Taking into account the difference in cost of cobalt as compared with nickel, I am satisfied the metal costs for plating a given quantity of work with cobalt, would be considerably less than for nickel plating a like quantity."

"Furthermore the use of cobalt bath XIII B equipped with automatic apparatus for conveying parts through the bath would reduce the labor cost 75 percent, such apparatus would be practical for a greater variety of wares than is now the case with nickel."

"We cannot speak too highly of cobalt bath XIII B, and con-

fidently believe its future history will surpass the history of any electro-plating bath now in general use."

"In conclusion, please accept my warmest congratulations upon your successes with cobalt solutions, and heartily appreciating the opportunity of testing these solutions, I desire to sincerely thank you, kind sir, for the benefits derived therefrom."

GENERAL CONCLUSIONS FROM COMMERCIAL TESTS ON COBALT PLATING SOLUTIONS.

I. Several cobalt solutions were found to be suitable for electro-plating with cobalt under the conditions of commercial practice. Best among these are the following:

Solution I B:

Cobalt-ammonium sulphate, $CoSO_4.(NH_4)_2SO_4.6H_2O$, 200 grams to the litre of water, which is equivalent of 145 grams of anhydrous cobalt-ammonium sulphate, $CoSO_4.(NH_4)_2SO_4$, to the litre of water. Sp. gr. = 1.053 at 15° C.

Solution XIII B:

Cobalt sulphate $CoSO_4$	312 grams
Sodium chloride NaCl	19.6 "
Boric acid	nearly to saturation
Water	1,000 c.c.

Sp. Gr. = 1.25 at 15° C.

II. Cobalt plates from these solutions, on brass, iron, steel, copper, tin, German silver, lead and Britannia metal articles, of different shapes and sizes, deposited under conditions identical with those met with in general nickel plating practice, are firm, adherent, hard and uniform. They may readily be buffed to a satisfactorily finished surface, having a beautiful lustre, which, although brilliantly white, possesses a slightly bluish cast.

III. The electrical conductivity of these solutions is considerably higher than that of the standard commercial nickel solutions, so that other things being equal, they may be operated at a lower voltage for a given speed of plating.

IV. Solution I B is capable of cobalt plating on the various sizes and shapes of objects met with in commercial practice at a speed at least four times that of the fastest satisfactory nickel solutions.

V. Solution XIII B is capable of cobalt plating on the various sizes and shapes of objects met with in commercial practice at a speed at least fifteen times as great as that of the fastest satisfactory nickel solutions.

VI. Plates from both of these solutions on various stock pieces, satisfactorily withstood the various bending, hammering and burnishing tests to which commercial nickel work is ordinarily submitted.

VII. These two very rapid cobalt solutions are remarkable for their satisfactory throwing power. That is, they readily and satisfactorily deposit the cobalt in the indentations of the work.

VIII. These two rapid solutions operate at these high speeds in a perfectly still solution without agitation of any kind.

IX. These solutions are both cleaner, that is freer from creeping salts and precipitated matter, than the standard commercial nickel baths.

X. The cobalt deposited at this rapid speed is very much harder than the nickel deposited in any commercial nickel bath. Consequently a lesser weight of this hard cobalt deposit will offer the same protective coat as a greater weight of the softer nickel deposit. Considering solution XIII B, operating at 150 amperes per square foot, on automobile parts, brass stampings, etc., etc., a sufficient weight of cobalt to stand the usual commercial tests, including buffing and finishing, is deposited in one minute. With the best nickel baths, it takes one hour, at about 10 amperes per square foot, to deposit a plate equally satisfactory. Therefore, the actual weight of metal on the cobalt plate must be approximately one-quarter that of the nickel.

XI. For many purposes, under the condition of these rapid plating solutions, one-quarter the weight of cobalt, as compared with nickel, is required to do the same protective work. Consequently, if nickel is worth 50 cents a lb., in the anode form, cobalt could be worth nearly $2.00 a lb., in the same form, to be on the same basis, weight for weight of metal. In addition there are other advantages of cobalt in saving of labor, time, overhead, etc.

XII. A smaller plating room would handle a given amount of work per day with cobalt than with nickel.

XIII. With these very rapid plating solutions, by the use of mechanical devices to handle the work, the time required for plating, as well as the labor costs may be tremendously reduced. Solution I B, and particularly Solution XIII B, are so rapid as to be revolutionary in this respect.

XIV. Obviously the cost of supplies, repairs, etc., would be less with cobalt-plating than with nickel-plating, as the size of the plant for a required amount of work is less.

XV. The voltage required for extremely rapid cobalt plating is greater than that for most nickel-plating baths; it is not so great but that the machines at present in use may in general be operated. For the same speed of plating, the cobalt solution requires much the lower voltage.

XVI. For a given amount of work the power consumption for this rapid cobalt work is less than that for nickel. This is obvious, because the total amount of metal deposited in the case of cobalt is very much less, whereas the voltage at which it is deposited is not correspondingly greater.

XVII. Ornamental work on brass, copper, tin or German silver would require only a one-minute deposit. Even wares exposed to severe atmospheric influences, or friction, could be admirably coated with cobalt in bath XIII B in fifteen minutes. The tremendous possibilities of this solution are not to be completely realized unless mechanical devices are applied to reduce hand labor to a considerable extent.

XVIII. Thick deposits from these solutions are vastly superior to any that we have seen produced from nickel solutions. The tendency to distort thin cathodes is less pronounced, while electrotypes and electro-dies have been given a superior thick deposit in a most satisfactory manner. The lines were hard, sharp and tough and the surface smooth. Nickel does not equal cobalt for excellence of massive plates.

XIX. Many of these tests were passed upon by uninterested skilled mechanics at the plant of the Russell Motor Car Company, who invariably reported in favor of the cobalt as above.

XX. Both baths I B and XIII B are substantially self-sustaining, once they are put into operating condition, and the amount of ageing required to do this is very much less for them than that for the present commercial nickel baths.

A number of automobile parts, and a large number of skates, cobalt plated, were turned out at the plant of the Russell Motor Car Company under Mr. Barrows' direction, and many of the skates have now (February 6, 1915), been under observation in actual use for several months.

On this date Mr. Barrows reported that skates plated from solution XIII B, many of which had had extremely hard usage in the hands of boys, etc., were showing up with surprising satisfaction.

There is absolutely no stripping of the plate along the edge of the skate, either before or after use, which, unfortunately is not uncommon with nickel-plated skates. Furthermore, the cobalt-plated skates seem to be decidedly superior to the nickel-plated skates as regards their resistance to corrosion. Another very noticeable feature about the cobalt-plated skates is that they are very free from scratches after rough usage as compared with nickel. That is to say, the cobalt plate is decidedly harder than the nickel plate. Most of the skates in question were plated in three minutes at 90 to 100 amperes per square foot. Nickel plates at the same plant are plated in one hour at about 4 amperes per square foot.

There is apparently considerably more cobalt metal plate on these skates than need be to make them equivalent to nickel-plated skates.

The numerous analyses in connection with these experiments were made by Mr. Russell C. Wilcox, and during the summer of 1914 a number of plating experiments were run by Mr. C. S. Allin. The authors acknowledge with thanks their indebtedness to these gentlemen.

Research Laboratory of Applied
Electrochemistry and Metallurgy,
School of Mining,
Queen's University,
Kingston, Ont.

December 15, 1914.

DISCUSSION.

C. W. Bennett (*Communicated*): This is a most interesting paper. We have all known that the statements in books concerning the use of cobalt instead of nickel were not correct, and it is gratifying to have these inaccuracies cleared up, and also gratifying to find that the electroplating industry will have a metal with which far more can be done than with nickel. We are particularly fortunate also in having along with the laboratory tests the several commercial tests of these solutions. Few of us realize how hard it is to do actual plating in the laboratory. It is hardly possible to obtain in the laboratory as good results as are obtained in actual practice. This statement seems to be contrary to accepted opinions, but I think electroplaters will bear me out in that. I have seen a lot of laboratory plating, but it has never compared equally with the plating done in the commercial plant. Of course in many cases where the change of the solution is to be watched closely, the reverse would be true, I hope to see electroplating with cobalt widely applied.

One interesting point in this paper is not explained. The solution of cobalt sulphate, which contains only a little greater quantity of cobalt, can be run at much higher rates of deposition in the presence of sodium chloride and boric acid. Since it seems to be impossible to get the people who are interested in nickel plating to explain the effect of such additions, it appears to me that Mr. Kalmus would advance our knowledge of electrodeposition, and furthermore, score heavily on the nickel people, if he could determine what the specific action of boric acid and sodium chloride is.

O. P. Watts (*Communicated*): I congratulate the authors and this Society upon the presentation here of the most interesting and what may possibly prove the most epoch-making paper contributed to the plating industry in recent years. The proposal to substitute cobalt for nickel in electroplating would appear to be the final word in the world-wide campaign among platers to speed up the process of nickel plating. Deposition at 150 amperes per square foot from a cold, still solution, and the production in three minutes of a coating which equals in appearance and excels in durability the best nickel plating would seem

to put cobalt in a class by itself so far as present plating practice is concerned.

There are three recognized methods of increasing the rate at which a good deposit can be obtained from any particular solution—increase the concentration of the solution, stirring, or heat. The maximum effect is of course obtained by a combination of the three methods. The surprising thing about these discoveries in cobalt plating is that so great an increase in speed has been secured by merely increasing the concentration of the solution.

Although zinc has been deposited by Pring and Tainton* at 465 amperes per square foot, the other metals are plated from cold, stationary solutions at current densities but a small fraction of that regularly used in these experiments. These facts, and the reported inferiority of a nickel bath of similar concentration and composition to the cobalt solution, raised the question: Are the splendid results obtained from the cobalt due to some specific property of cobalt, or are they due to the extremely great concentration of the solution and therefore obtainable with other metals? To answer this question deposits of several metals have been made from very strong solutions, and four samples of these deposits are exhibited.

Sheets of brass and of copper were polished, immersed for a minute in the electric cleaner, rinsed, and hung in the plating bath. They were then rinsed, the lower half of each deposit was buffed, treated in the electric cleaner, rinsed and dried.

Iron was deposited for two minutes at 197 amperes per square foot (2,200 per sq. m.) from a nearly saturated solution of the mixture of ferrous sulphate, ferrous chloride and ammonium chloride which is used for refining iron in the chemical engineering laboratories of the University of Wisconsin. A smooth, handsome deposit was obtained, which adhered perfectly.

A copper solution comparable to the best cobalt bath should contain over 120 grams of metal per liter. Since a cold, saturated solution of copper sulphate contains only about 70 grams of copper per liter, the metal concentration was increased by the addition of copper nitrate. After adding 20 c.c. of strong nitric acid, copper was deposited for two minutes at 163 amperes per

* Tr. Amer. Electrochemical Soc., **25**, 295 (1914).

square foot (1,800 per sq. m.). The plate was satisfactory in every respect, showing no signs of burning.

For the deposition of nickel 300 grams of nickel chloride, and 60 grams of boric acid were stirred in a liter of water. Considerable boric acid remained undissolved. At an average of 170 amperes per square foot (1;870 per sq. m.) for two minutes this solution gave a deposit that was good except at the bottom, where the current density was above the average. Here the deposit peeled.

A cobalt bath was prepared by adding 30 grams of boric acid to the residues of a half dozen different cobalt baths used by a former student when studying cobalt plating. In six minutes at 160 amperes per square foot (1,760 per sq. m.) this gave an excellent deposit. In spite of the fact that this bath was so strongly acid that the current efficiency was very low, and there was a violent evolution of hydrogen, the deposit was tough and perfectly adherent.

These rather hurried experiments show that good deposits of other metals may be obtained at the same rate as for the cobalt solution. It is probable, however, that the nickel solution would give trouble if operated for any length of time at such extreme current densities on the anode.

The throwing power of all except the cobalt bath was good, as shown by deposits on the back of the sheets. The poor throwing of this cobalt solution is accounted for by its acidity, as a test showed that below ten amperes per square foot (110 per sq. m.) no deposit appeared in two minutes. May not the excellent throwing power of these three solutions, of Dr. Kalmus' cobalt solutions, and of the usual cyanide copper solution, be due to their use at current densities which are higher in regard to their metal concentration than the usual practice for the poor-throwing acid copper solution? Can not some member of the Society throw light upon this question?

An interesting observation was the evolution of gas from the nickel and iron deposits when they were immersed in hot water. From the iron the evolution was as vigorous as if the metal had been dipped in an acid, and lasted a half minute or more. Less gas came from the nickel, and none was observed from the

cobalt or copper plates. It looks as if the high current density was responsible for these excessive quantities of absorbed gas. I should like to ask Dr. Kalmus if he ever observed any evolution of gas when cobalt-plated articles were rinsed in hot water. I find from Moissan's *Chimie Minerale* that on cooling the heated metals in an atmosphere of hydrogen, cobalt absorbs one-tenth and nickel one hundred volumes of this gas.

The brittleness, curling, and peeling of nickel deposits is generally conceded to be due to absorbed hydrogen. The unfortunate tendency of the nickel anode to become passive on the slightest provocation and start to manufacturing acid in the plating solution has long been a bugbear to the nickel plater, and it is now the general practice to inoculate the nickel solution with a generous dose of the slightly dissociated boric acid as a preventive against the presence of a more strongly dissociated acid, which would result in a still more vigorous evolution of hydrogen and the peeling of the deposit.

Dr. Kalmus' experiments show that his cobalt anodes do not become passive even in a pure sulphate solution at extremely high current densities. The great superiority of cobalt over nickel for electroplating lies in its not absorbing hydrogen, with the production of brittleness and curling, and in the impassivity of the cobalt anode.

Whether or not cobalt will displace nickel for plating is entirely a question of the relative prices of the two metals. At the present ratio of four to one the economy of cobalt is by no means clear.

Cold nickel solutions similar to XIII B, but weaker in metal, are in successful use at 20 amperes per square foot (220 per sq. m.), or one-eighth the average speed of the cobalt solution. According to current prices in a plating-trade journal, 1,000 gallons of this solution would cost as follows:

1,000 lb.	nickel sulphate	@ 20c	$200.00
312 "	boric acid	" 8c	24.96
250 "	salt	" 1c	2.50
			$227.46

Allowing for cobalt sulphate only the cost of the metallic cobalt in it, 1,000 gallons of bath XIII B as given on page 100 would cost:

5,610 lb.	cobalt sulphate (1,176½ lb. metal)	$2,353.00
421 "	boric acid	33.68
204 "	salt	2.04
		$2,388.72

Although equipment of the two solutions with anodes will lower the ratio of costs, it will raise the total cost of the cobalt solution to an amount that is likely to produce instant paralysis of the pocketbook of the prospective purchaser.

It is to be hoped that the price of cobalt will soon drop to a point where platers may enjoy the fruits of Dr. Kalmus' valuable investigations, and be forever freed from the burning and peeling of nickel deposits and the doctoring of sick nickel baths.

C. G. Fink: Before entering the lecture room I was going to offer a suggestion of my own, but I am a bit discouraged after seeing the work on cobalt-nickel separation shown by Dr. Smith. I understand that the nickel deposits are decidedly yellow and the cobalt deposits are decidedly blue, and it occurred to me, could not we combine the two and make a cobalt-nickel alloy deposit?

George B. Hogaboom: That has been done.

C. H. Proctor: I would like to say a word or two on the cobalt situation. During the symposium of the American Electroplaters' Society in connection with the American Electrochemical Society at Atlantic City two years ago, the matter of deposition of cobalt was brought up, and I believe I made the statement that until the price of cobalt came down very close to that of nickel, it would not be of any commercial value to the electroplater. At the present time I understand the single nickel salts which contain about twenty-one to twenty-two percent nickel are being sold for eight and one-quarter cents per pound, while on the other hand, the cobalt sulphate would cost fifty cents per pound, and there is quite a difference in the ratio of the cost of anodes, that of nickel $0.45 and cobalt $1.50 per pound.

It would be interesting if the authors carry their experiments further and ascertain if it is possible to deposit cobalt direct on zinc and its alloys. A perfect deposit of nickel was obtained from a regular nickel solution containing an addition of magnesium sulphate and with the use of steel anodes. The same articles plated in this solution were then placed back in the ordinary solution, and in a moment or two black streaks developed. Again they were immersed in the solution containing the magnesium sulphate, with the steel anodes, and in a few moments they became white and bright again. This leads me to believe that something might be accomplished along these lines with cobalt, nickel and iron.

It might be interesting to see if it is possible to deposit cobalt directly on a zinc surface or a combination zinc alloy surface, because if a satisfactory deposit can be obtained without much trouble I am sure it would be very interesting to the electroplating industry. The high cost of cobalt at the present time eliminates cobalt from the platers' consideration as a commercial commodity unless its economic utility is proven in practice.

George B. Hogaboom: This paper is probably one of the many good results of the symposium on electroplating which this Society held two years ago. It has that peculiar value, which is so often lacking, in that the work of the scientist has been corroborated by the practical man under commercial conditions. Dr. Kalmus and his associates who did the research work and Mr. W. S. Barrows who put the data obtained to the test of practical use such as any electrodeposited articles must stand, are to be commended for their success. Such work as theirs will do much toward reducing the arbitrary methods of the rule-of-thumb plater to a scientific basis, the result of which would mean much to the electroplating industry.

The rapidity of the deposition of cobalt from the solutions given far exceeds that of any plating solution used at the present time, and if the deposit will withstand the wear and atmospheric conditions better than nickel it seems that it will in time be universally used.

We are of the opinion that solutions of such high density will be found to be unnecessary for commercial work. The initial expense of installation and the loss of solution through removing

work from the tank are against the use of solutions containing so much salt.

Mr. C. H. Buchanan and his associate Mr. Thomas B. Haddow conducted several tests with solutions containing only six ounces of cobalt ammonium sulphate and obtained a deposit of 0.001 inch (0.025 mm.) in ten minutes. From a plater's point of view, that would be the better solution to use; it would give ample time to change batches of work; the cost of the mechanical loss of the solution would not be excessive, and, still the rate of deposition would be such as to make it a more profitable bath to operate than any of the present nickel solutions. Another great advantage would be that there would not be so great an amount of capital tied up.

William Blum: I wish to call attention to the statement regarding the manufacture of electrotypes 1/16 inch (1.5 mm.) thick. At the present time the Bureau of Standards is making a study of some of the problems of electrotyping in connection with the Electrotypers' Association. In a nickel electrotype, where a deposit of nickel is used on the surface, at present it is difficult to obtain a satisfactory deposit much more than 0.001 inch in thickness (0.025 mm.), and that usually requires from one to two hours. These deposits are produced on graphited wax surfaces, where there is little adherence to the surface, and as soon as the deposit goes over 0.002 inch (0.05 mm.) there is a tendency toward cracking and curling. The statement that cobalt electrotypes can be made many times as thick as the present nickel electrotypes is therefore of great interest to the electrotyping industry.

W. Lash Miller: It would be a mistake to conclude that cobalt must be as cheap per pound as nickel before it can displace it, because on page 111 the authors say: "This man buffed the cobalt plates upon a 10-inch cotton buff wheel revolving at 3,000 revolutions per minute. The finish was perfect with no edges exposed. These stampings have been plated in two dozen lots for one minute, and from a total of five hundred we have found but three stampings imperfect after buffing." That is, 1 minute in the cobalt bath replaced 75 minutes in the nickel bath. On the next page they say that the current density they used was

about fifteen times as great as that for the usual nickel bath. If the nickel bath is 100 percent efficient, and they say that the cobalt here is 99 or 100 percent efficient, it means that the cobalt on the casting was only one-fifth of the amount of nickel they were accustomed to put on. That would bring the effective price of nickel in competition with cobalt up from $0.40 to $2 a pound, which is "a wonderful confirmation of the theory." I do not know for sure whether a plater charges any more for leaving an article in the bath one and one-quarter hours than for one minute, but it seems likely that he would.

PRESIDENT LIDBURY: That interesting subject is the whole thing.

W. LASH MILLER: If there is anything in the claim that less cobalt will do for these cheaper articles, we ought to know it. If the buffer does not recognize the difference between heavy and light plating, that might affect the proposition.

H. C. CHAPIN: In connection with the rusting of cobalt I wish to call attention to a statement of Richards and Baxter, Proc. Am. Acad. **34**, 359 (1899), that cobalt should rust more easily than nickel because its lower oxide hydrates more readily than that of nickel. Thus cobalt may go into solution as cobaltous hydrate in water upon its surface, and may then be oxidized and precipitated as cobaltic hydrate, leaving the water free to dissolve more cobalt. Whitney, J. Am. Chem. Soc. **25**, 394 (1903) demonstrated such action in the case of iron by allowing specimens to stand under pure water for weeks, during which no visible change occurred, then admitting air which immediately caused cloudiness and yellow color in the liquid. Before assuming that cobalt resists rusting as well as nickel it might be well to compare specimens prepared in the same way, so as to prevent compensating differences in hardness, porosity, etc., from masking differences characteristic of the metals themselves.

GEORGE B. HOGABOOM: I have a sample of a piece of cobalt exposed to the fumes of a compound nitric and sulphuric acid bath for eighteen hours and then run over the buffer, and it has as good a color as it originally had. It had a 0.001 inch (0.025 mm.) deposit in twenty minutes from a double sulphate of cobalt with magnesium.

F. A. LIDBURY: How far is the superior nature of the deposits from cobalt, as compared with the ordinary results of nickel plating, due to the fact that they have been prepared from solutions which have not been operated for months, years or generations, and consequently have not obtained that beautiful degree of variability in composition and of impurity which was the object of so much discussion in our last symposium on electroplating in connection with nickel baths?

JOS. W. RICHARDS: This question of cobalt being more expensive than nickel is probably one which will solve itself. The Canadian deposits, as I understand, contain much more cobalt than can be at present commercially used. If, therefore, the cobalt can be cheaply separated by a metallurgical or electrometallurgical process, there is no reason why its price should not come down to approximately the price of nickel. I think that is the commercial situation.

C. G. FINK: I should like to add to Prof. Richards' remarks that the price of cobalt will come down as soon as the platers increase their demand. The steel people do not want cobalt. It is up to the platers to bring the price down, by increasing the consumption.

HERBERT T. KALMUS (*Communicated*): I regret extremely that business duties elsewhere made it impossible for me to be present at the last meeting of the American Electrochemical Society, to read in person our paper entitled "Electroplating with Cobalt." It would have been a great pleasure to me, as well as a source of no little enlightenment, to have listened to the very interesting discussion which followed the reading of this paper.

As I have already stated . . . "This paper is concerned with the presentation of a very large amount of experimental data on cobalt plating. It attempts to record data, to summarize, and to draw conclusions with reference to cobalt plating and its application in the industries. Theoretical considerations concerning the explanation of the results are reserved for a separate publication." Several of the points raised in the discussion will be treated in a subsequent publication of a more theoretical character, and any statement which I might make with regard to

these particular points at the present time would simply foreshadow what we expect to discover experimentally.

Some points mentioned in the discussion will be found to be touched upon, if not answered, by reference to a more complete paper published in the "Journal of Industrial and Engineering Chemistry," volume 7, May 1915, pages 379 to 399. A still more complete publication of the work is now in press, and will appear as a bulletin from the Bureau of Mines, Canadian Department of Mines, Ottawa, Canada.

I should like to add the following to the remarks made at the close of the reading of the paper.

We recognized from the outset that the cost of cobalt is not likely to be comparable with that of nickel, pound for pound, in the near future, and that consequently, to serve our purpose, we must find commercial uses for cobalt such that it does not simply substitute equivalently for nickel, but such that it serves a purpose which nickel will not serve.

Whatever may be true of other metals, so far as I know, no one has been able to deposit nickel, under satisfactory commercial conditions, at a rate in excess of 10 to 20 amperes per square foot (110 to 220 per sq. m.). We are able to plate cobalt at 150 amperes per square foot (1,650 per sq. m.), under commercial conditions. Comparing the two, we find that to plate a skate, for example, approximately one minute in the cobalt bath will give a protective coating as satisfactory as a regular 60 to 75 minute run in the standard nickel bath. In many respects the cobalt coating is more satisfactory than the nickel one, and in no respect does it seem to be less satisfactory. The point is, therefore, that we are plating about 15 times as rapidly but only about one-sixtieth as long, and consequently we use only approximately one-quarter the weight of cobalt metal that we use of nickel.

We must, therefore, not compare the market prices of nickel and cobalt, pound for pound, but rather their price efficiencies. So far as the consumption of anodes is concerned, this seems for many purposes to be distinctly in favor of cobalt.

This point seems to have been made by Professor Miller in the discussion.

As Professor Watts points out by his experiments, it is not difficult under suitable conditions and for a brief time, to plate a number of metals at 150 amperes per square foot (1,650 per sq. m.), or even at higher current densities. That, however, is not the problem, but rather, can nickel be plated continuously and under commercial conditions at any such high current density? The answer, I believe, is that it cannot, or at any rate, that it has not been as yet.

It may be, as Mr. Lidbury points out, that the superior nature of the deposits from cobalt solutions, as compared with commercial nickel solutions, is in part due to the fact that the solutions have "not been operated for months, years, or generations, and consequently have not obtained that beautiful degree of variability in composition and of impurity," which we must attribute to many commercial nickel baths. It will take years or generations to answer this point finally, but at the present time it is answerable for months and a single year. We have had the cobalt baths I B and XIII B operating more or less continuously through a period of months, aggregating more than a single year, and we have observed no tendency to cumulative detriment.

As regards the corrosion of the deposits upon ageing in the atmosphere, it would seem that there was very little, if anything, in favor of one or the other, as between nickel and cobalt. I have before me objects which were plated by us with cobalt more than two years ago, which have been standing in the ordinary atmosphere of an office since then, and which might have been nickel plated, so far as any observation of corrosion or color is concerned.

This brings me to speak of the point raised by Mr. Fink, to the effect that nickel deposits are decidedly yellow and cobalt deposits decidedly blue. This may be true under certain conditions, but as a general observation, at least for the 16 types of solutions which we have studied, it is not so. Cobalt plates may be said to have a slightly more bluish cast than nickel plates, but this difference is so slight that it would not be noticed by a casual observer.

Professor Watts makes the point that the initial investment for 1,000 gallons of our Solution XIII B would be a great

burden to the plater. There is no denying the fact that the initial investment for 1,000 gallons of Bath XIII B would be greater than the initial investment for 1,000 gallons of the standard nickel bath. However, I think that the difference need not be nearly so great as the figures given by Professor Watts would indicate. He has computed 1,176½ pounds of metal at $2.00 per pound. Starting with fairly pure cobalt oxide, reducing the oxide to metal, melting the metal, and casting same in the form of anodes, the final cobalt in anode form probably could be purchased today at $1.25 per pound. With a substantial market for cobalt sulphate in the plating industry, calculations based even upon this figure should be considerably too high. I consider $1,500 to be the outside estimate of what it would cost to put in 1,000 gallons of Bath XIII B, as against the estimate of $2,388.72, given by Professor Watts. I should like a contract to supply materials for fifty 1,000-gallon baths of Solution XIII B at $1,500 apiece!

Moreover, the entire cost argument of Professor Watts is based upon the hypothesis that as many 1,000-gallon tanks of cobalt solution would be required for a given installation as are required of nickel solution. As a matter of fact, one 1,000-gallon tank of cobalt solution, even with hand labor, due to the very much diminished time of plating, would turn out as much as several 1,000-gallon tanks of nickel solution. With mechanical devices for handling the work to get the benefit of the speedy plating of the cobalt bath, it is not clear but that the actual cost of installation for cobalt plating would be less than that for nickel plating.

It is my opinion that we may look for a diminished cost of cobalt metal and cobalt supplies as they find their way into the industries.

We have made no observations which would indicate that the throwing powers of Solution XIII B or I B were other than extremely satisfactory.

Answering Professor Watts' question, I would say that I have never observed considerable evolutions of gas when cobalt-plated articles were rinsed in hot water, nor have I had any serious difficulty with cobalt anodes, as a result of their becom-

ing passive, due to development of acid during the process of plating.

Due to limitations of space, only two solutions, I B and XIII B were reported upon for publication in the Transactions of the American Electrochemical Society. In the Journal of Industrial and Engineering Chemistry, and in the Bulletin of the Canadian Bureau of Mines, both referred to above, may be found details of experiments on 16 different types of solutions, among them Solution X, composed of cobalt ammonium sulphate and magnesium sulphate. Also experiments are described plating on zinc. These points bear upon the remarks of Mr. C. H. Proctor.

In connection with the remarks of Mr. George B. Hogaboom, to the effect that plating, as rapid as is possible with these cobalt baths, is not of commercial advantage, because it allows too little time for the operator to change batches of work, and because the mechanical loss of the solution would be excessive, I would point out that, while this may all be true to some extent, for the present method of handling the work, such speedy solutions as are now offered would warrant the adoption of entirely different methods. If these solutions came to be employed on a substantial scale it would not be hard to devise mechanical means for handling the work, which in many cases would amount to very little more than dipping. Thus a large saving would be effected in the labor and another saving effected in the amount of installation required for a given output of work.

The remarks in reply to Professor Watts in connection with the cost of installation of cobalt baths are also pertinent in reply to Mr. Hogaboom.

In connection with various remarks, and particularly those of Dr. Miller, with regard to heavy *versus* light plating, I would add that no doubt one of the reasons that something like one-quarter the weight of cobalt as compared with nickel will serve to give an apparently equally efficient protective coating, is because the cobalt plate is actually very much harder and denser. This is to be expected from the relative rates of deposition.

A paper presented at the Twenty-seventh General Meeting of the American Electrochemical Society, in Philadelphia, at a Joint Session with the American Electroplaters' Society, April 24, 1915, President F. A. Lidbury in the Chair.

ELECTRODEPOSITION OF SMOOTH SOLID LEAD FROM LEAD NITRATE SOLUTIONS.

By Frank C. Mathers and Asa McKinney.

Summary.—The electrolysis of solutions of lead nitrate produces a mass of loose crystals upon the cathode. Certain experimenters[1] have claimed to have improved the deposit by the use of addition agents, though in at least one of these cases Betts[2] has been unable to repeat the results.

The authors have succeeded in obtaining as smooth coherent lead deposits from lead nitrate solutions as from any other lead bath.

The best composition of the bath is: 10 percent lead nitrate, 2.5 to 5 percent acetic acid and 1 percent of the residue from the commercial extraction of Curaçao aloes in the manufacture of aloin. Crude aloes may be used in the place of the aloes residue but the deposits are not as good. The aloes or the residue should be dissolved by warming in the acetic acid before adding the lead nitrate solution. The bath should not be filtered before using. A current density of 0.4 amp. per sq. dec. (3.7 amp. per sq. ft.) may be used.

Free acetic acid is necessary in the bath to avoid the formation of basic salts. Free nitric acid in place of the free acetic acid greatly hastens the deterioration of the baths, and the greater the concentration of the acid the quicker the deterioration of the baths.

A number of addition agents were tried but none approached the residue from Curaçao aloes in efficacy. The aqueous extract of poplar wood, which gave excellent deposits in acetate baths, was not satisfactory in these nitrate solutions.

[1] Jarvis and Kern, Trans. Amer. Electrochem. Soc., **15**, 453 (1909); Tucker and Thomssen, *Ibid.*, **15**, 477; Matuschek, Austrian Pat. 5,766 (1909) and D. R. P. 239,222 (1910); Glaser, Zeit. Electrochem., **7**, 365 and 381 (1900-01).

[2] Trans. Amer. Electrochem. Soc., 6, 35 (1904).

The baths have a life of only six or seven weeks, after which the deposits become spongy and non-adherent; consequently it seems unlikely that this nitrate bath can have any practical use. No way was found to overcome this deterioration of the baths.

A rough but not spongy deposit shows the exhaustion of some constituent of the bath. Warming the bath for a few minutes will bring more of the aloes residue into solution and correct any trouble due to lack of addition agent. Sometimes more acetic acid must be added to replace that which has been used in chemically dissolving the lead.

Manipulation.—A cathode of thinly rolled lead was suspended between two lead anodes in a bath containing 200 cc. of the solution. The current density was 0.4 amp. per sq. dec. (3.7 amp. per sq. ft.). Electrolysis was at room temperature. The cathodes were 5 by 5 cm. (1.9 by 1.9 in.) and the anodes 3.5 by 4 cm. (1.4 by 1.6 in.). The cathodes were cleaned by dipping in nitric acid before placing them in the baths. A cleaner, brighter surface was obtained in cleaning those cathodes which were made from lead containing some mercury. The lead anodes were either amalgamated or wrapped in filter paper to prevent slime reaching the cathodes and producing rough places. The anodes were suspended by copper wires which did not dissolve during the electrolysis.

Effect of Various Addition Agents.—Of the addition agents which were tried, the residue of gum which remained after the extraction of Curaçao aloes in the commercial manufacture of aloin was vastly superior to any other. A sample[3] of this residue was furnished to us by Sharp and Dome, manufacturing chemists, Baltimore, Md. This is the addition agent that gave such excellent results in the deposition of lead from lead acetate[4], lead lactate[5] and lead formate[5] solutions.

The baths used in testing the effect of addition agents contained 10 percent lead nitrate, 4 percent sodium nitrate, 5 percent acetic acid and 0.5 percent of the addition agent except in the case of liquid addition agents, where 4 drops were added to each 200 cc.

[3] A few experiments were tried with a sample of residue which was obtained from the Norwich Pharmacy Co., through the assistance of the New York Quinine and Chemical Co., both of New York. This residue contained more water-soluble material and gave rougher deposits than the sample from Sharp and Dome.

[4] Mathers, Trans. Amer. Electrochem. Soc., 26, 99 (1914).

[5] Mathers and Cockrum, *Ibid.*, 26, 117 (1914).

bath. The solid addition agents were dissolved as completely as possible by warming in the acetic acid and the solution thus obtained was added to the bath. The following substances, besides the aloes, were tried as addition agents: Galbanum, sandarac, saponin, benzoin, guaiac, euphorbia, myrrh, garcinia hamburii, eucalyptus rostrata, pterocarpus marsupium, tragacanth, balsam tolu, manna, gambir, gamboge, convolvulus scammonia, asafetida, mastic, lycopodium, terbene, caramel, casein, catechu, ammoniac, terpin hydrate, menthol, tannigen, phloridzin, salicin, gum arabic, formaldehyde, mace, glue, agar-agar, nitroso β-naphthol, licorice extract, and the essential oils of clove, cedar, eucalyptus, juniper, sandalwood and sassafras. In almost all cases the deposits were crystalline or spongy and non-adherent or rough. The deposits with the licorice and the phloridzin were smooth for about two days, after which they became non-adherent and finally spongy.

Deterioration of the Baths.—Baths acidified with nitric acid rapidly reached a stage after which only spongy deposits could be obtained. Even with the addition of aloes residue a fair deposit could be produced only for a few days. Substitution of acetic acid for free nitric acid greatly lengthened the life of the baths.

Deterioration took place in the case of the best baths after seven weeks' continuous electrolysis. The further addition of aloes residue, of acetic acid, also of formaldehyde (0.5 to 2.5 percent by volume of the 40 percent solution), hydrogen peroxide (0.5 to 15 percent by volume of the 3 percent solution) and ammonium nitrate (2 percent) produced no important improvement in the deteriorated baths, though slight improvement was obtained with the hydrogen peroxide. Some of these additions were tried because it was suspected that nitrous acid, which was found in appreciable quantities in deteriorated baths, though also in traces in baths in good working order, might be the cause of the deterioration. New baths deteriorated in forty-eight hours after the addition of 0.15 percent of sodium nitrite; this deterioration was not prevented by the addition of formaldehyde, urea, or ammonium nitrate, but was prevented by the addition of 5 to 10 percent by volume of 3 percent hydrogen peroxide.

Hydrogen peroxide added to new baths lengthened their life only slightly.

Composition of Baths.—The effect of variation of individual constituents was tried on a bath containing, except as stated, lead nitrate 10 percent, sodium nitrate 4 percent, acetic acid 2.5 percent, Curaçao aloes residue 0.5 percent.

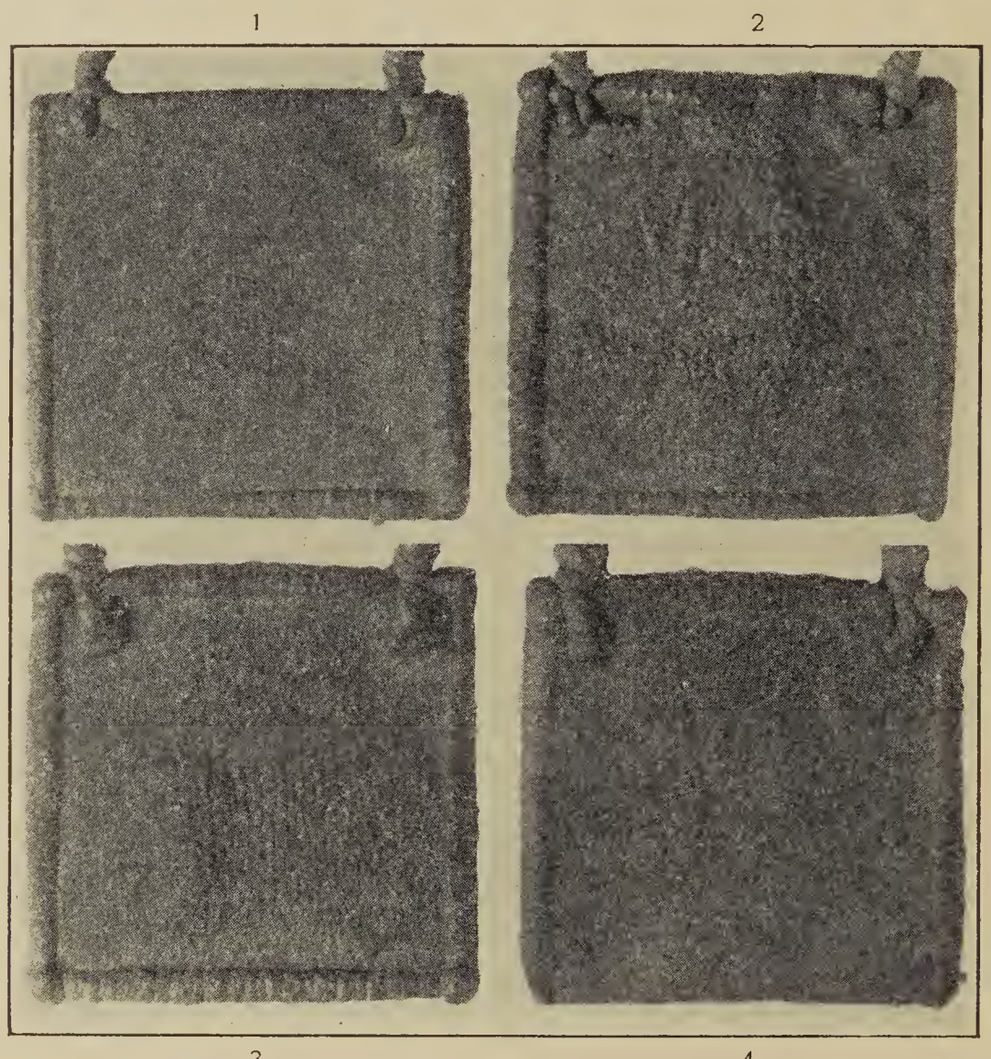

FIG. 1.

The baths from which these lead cathodes were obtained were as follows:

1. Lead nitrate, 5 percent; sodium nitrate, 2 percent; acetic acid, 2.5 percent; Curaçao aloes residue, 1 percent.
2. Lead nitrate, 20 percent; sodium nitrate, 2 percent; acetic acid, 2.5 percent; Curaçao aloes residue, 1 percent.
3. Lead nitrate, 10 percent; sodium nitrate, 0 percent; acetic acid, 2.5 percent; Curaçao aloes residue, 1 percent.
4. Lead nitrate, 10 percent; sodium nitrate, 16 percent; acetic acid, 2.5 percent; Curaçao aloes residue, 1 percent.

Variation of lead nitrate: 3 percent rough and slightly spongy; 5, 10, 20 and 25 percent excellent but with life (as regards time until deterioration) decreasing and degree of smoothness increasing with increase of concentration. The 10 percent lead nitrate

bath seemed most generally suitable, giving deposits sufficiently smoother than the 5 percent bath to compensate for its slightly shorter life.

Variation of sodium nitrate: No improvement from 0 to 16 percent; shorter life with the larger amounts; this constituent should therefore be omitted.

Variation of acetic acid: Without acid the deposit was black and spongy; with 2.5 to 5 percent good, the latter being somewhat the better; with increasing percentages up to 50 the deposit became slightly rougher and the life shorter.

Variation of Curaçao aloes residue: No variation in initial results with baths containing 0.05 to 1.5 percent. Roughness of deposit sets in in order of dilution, the bath containing the largest amount of aloes giving the best deposit for the longest time. One percent should be used, since with larger quantities the insoluble matter in the bath is sufficient to make the cathodes rough. Baths which are giving rough deposits owing to exhaustion of the aloes residue in solution may be improved by heating to boiling, which brings more of the aloes residue into solution.

Current Density and Voltage.—A higher current than 0.4 amp. per sq. dec. (3.7 amp. per sq. ft.) should not be used. A current of one ampere produced rough deposits and hastened the deterioration of the baths. A bath that would have produced good deposits for 5 or 6 weeks at 0.4 amp. deteriorated and gave spongy deposits in 6 to 8 days when electrolyzed at 1 amp. per sq. dec.

With a bath containing 5 percent acetic acid, 5 percent lead nitrate and 0.5 percent Curaçao aloes residue, the voltage averaged 0.35 with a current of 0.4 amp. and the anode and cathode about 2 cm. (0.79 in.) apart.

Current Efficiency.—In a series of measurements which were made daily for a period of ten days on a bath containing 5 percent lead nitrate, 5 percent acetic acid and 0.5 percent Curaçao aloes residue, the observed variations from theoretical cathode efficiency lay within the limits of experimental error, averaging 99.98 percent, while the anode efficiency, as is the case in all lead baths,[6] was appreciably over the theoretical value, averaging 100.6 per-

[6] Mathers, Trans. Amer. Electrochem. Soc., 17, 266 (1910).

cent. The anodes, made of once electrodeposited lead, were amalgamated on the surface, hence the high anode efficiency is not due to mechanical loss.

Properties of the Cathodes.—The specific gravity of the cathode which was deposited from the bath containing 10 percent lead nitrate, 10 percent acetic acid, 1 percent Curaçao aloes residue and 4 percent sodium nitrate, was determined with a pycnometer at 20° C. A section of the cathode containing the starting sheet gave the value 11.32, while material from which this starting sheet had been sawed away gave values of 11.32 and 11.33. This latter material after melting and casting showed a specific gravity of 11.36. These results show that lead electrodeposited from the nitrate solution is very dense.

The cathodes are brittle and hard. These properties are probably caused by the comparatively large quantities of addition agent that is absorbed, while in the cases of the fluosilicate and perchlorate baths where only small quantities of the glue and clove oil are used, the cathodes are tough and soft. No attempt was made to determine the quantity of addition agent in the cathodes.

An attempt to determine the nitrate in the cathode lead, caused by inclusion of the electrolyte in the deposit, was made by a method which has been used[7] in testing silver deposited in a silver coulometer. Four grams of the lead cathode, in the form of fine cuttings obtained with a hack-saw, was treated with 6 to 8 gms. of mercury and two drops of sulphuric acid. This mixture was warmed for a few minutes and filtered. The filtrate was tested for nitrate by the phenol-sulphonic acid method used in water analysis. The color was browner than the standard, hence only an approximate comparison was possible. The average of several determinations showed 0.0024 percent of lead nitrate. The mercury may not have released[8] all of the nitrate (further treatment of the amalgam gave no appreciable quantities of nitrate), nevertheless the result indicates that only small amounts of the electrolyte are included in the lead deposit.

[7] Rosa, Vinal and McDaniel, Elect. World, **63**, 374 (1914); Bur. Standards Bull., **10**, 520 (1914).

[8] Richards and Anderegg, Jour. Amer. Chem. Soc., **37**, 10 (1915).

Remarks: This work was taken up for the purpose of obtaining more information upon the question of the use of addition agents in metal deposition. Until recently it was supposed that solid lead deposits could be obtained only from baths containing lead salts of perchloric acid or of a fluorine acid such as fluosilicic, fluoboric, etc., with the proper addition agent in each case. The good behavior of these baths was supposed to depend upon the fact that the acids in them were strongly dissociating and non-oxidizing. This last property was added to exclude nitrate baths because it was known that lead nitrate solutions gave crystalline, non-adherent deposits although nitric acid is a very strongly dissociating acid. Solutions of lead acetate or lactate or formate were supposed to be unsuited for the deposition of lead because these organic acids were very weakly dissociating. However in previous papers[4-5] it has been shown that solid deposits of lead can be obtained from solutions of the lead salts of these weak acids. It was desirable to find out the conditions for obtaining good deposits from lead nitrate solution in order to make plain the fact that solid deposits of lead may be obtained from the lead salts of any acid whatever, regardless of whether it is weak or strong, oxidizing or non-oxidizing, organic or inorganic. The important thing is to use the proper addition agent for the particular salt in question. This theory, which was advanced in an earlier paper,[9] now seems proved, since a lead salt of each kind or class of acids has been made to yield a good deposit.

Glue is used as addition agent in the fluosilicate or fluoborate baths, but it gives only fair deposits in the perchlorate bath and is entirely unsatisfactory in the acetate and nitrate baths. Clove oil is the best addition agent in the perchlorate bath and seems to be as good as the glue in the fluosilicate, but is worthless in the acetate of the nitrate baths. Extract of poplar wood, obtained by boiling the wood in water, is of little value in the nitrate solutions, but it gave excellent deposits in the acetate baths. Aloes gave peculiar projections on the cathode in the perchlorate baths, but it is the best addition agent in the nitrate or acetate solutions. These facts point to the great effect which the negative or acid radicle has upon the deposits, otherwise an addition agent

[9] Mathers, Trans. Amer. Electrochem. Soc., **24**, 315 (1913).

that gave a good deposit in one lead bath would give an equally good deposit in all other lead solutions.

No work was done to try to determine why these particular addition agents produced the good deposits.

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DISCUSSION.

C. W. Bennett (*Communicated*): It was pointed out[1] that colloids tend to decrease the crystal size, therefore enhancing the value of a deposit of lead from an acetate solution, and that also if the conditions were right, colloids had this effect generally in the deposition of lead and the other metals for that matter. We know that the size of the crystals obtained depends upon the rate of deposition, the voltage between the cathode and the solution, the temperature, and the presence of the colloid of the proper nature to affect the crystal size. This latter Mr. Mathers has found in a specific case by actually trying a large number of addition agents, which gives the report the appearance of a pharmacopoeia. What I should like to see done is the determination of the character of addition agents to be added in a specific solution with a specific metal, so that it could be applied generally, not requiring a whole set of experiments, as Mr. Mathers has prepared here, in changing from the acetate to the nitrate solution. I have asked Mr. Bancroft to give us a word as to the method of attack.

W. D. Bancroft (*Communicated*): The general theory of the effect of colloidal addition agents is so simple that it is a pity that Mr. Mathers does not apply it in some special cases, instead of continuing to collect interesting but purely empirical information. A colloidal addition agent must be carried to the cathode by the current and must be adsorbed by the precipitating metal in such amounts as to cut down the size of the crystals without giving rise to pulverulent metal. Whether the colloid will be carried to the cathode or not will depend on the nature of the colloid, the temperature, the degree of acidity, and the

[1] Trans. Am. Electrochem. Soc., **21**, 236 (1912).

nature of all the ions in the solution. The extent to which the colloid will be adsorbed by the metal will depend on all these things and on the nature of the metal. There is nothing surprising theoretically in the fact that a given addition agent does not work equally well in different baths for the same metal. Mr. Mathers ought to have been able to predict that. If he will try adsorption experiments with a large metal surface he can confirm his electrolytic results by experiments not involving the passage of a current. What we do not know, however, is whether it is essential or even desirable that the colloidal addition agent should adsorb the ion of the metal as well as be adsorbed by the metal itself. I doubt the necessity of it; but I do not as yet see any way of predicting this conclusively. However that may be, the study of colloidal addition agents has reached the point where quantitative experiments with colloidal metals are absolutely essential. It seems to me that Mr. Mathers ought to make these experiments.

President Lidbury: I am glad that Prof. Bancroft has made this comment on Dr. Mathers' work, because it has seemed to me a great pity that Dr. Mathers should be spending such a tremendous amount of time and energy in collecting data which really do not take us very far, instead of devoting himself to the investigation of underlying principles. I venture to hope that these comments of Prof. Bancroft will be very seriously considered by the author.

Lawrence Addicks: I wish to suggest that Dr. Mathers may have gotten the deposit once, but was he able to do it twice? I had occasion several months ago to try to protect from corrosion some copper leads. I wanted to plate them with lead, but as I did not have handy the materials to make the better-known fluosilicate solution, I took this paper as a guide. However, I got a deposit that would discourage the most enthusiastic experimenter. The trouble was of course in the extract. There is a good deal of difference in the quality of woods we get from different sources, and it seems to me if Dr. Mathers could specify more accurately and definitely concerning, say, pyroligneous acid, or other active reagents, the whole matter would be in better shape.

F. C. MATHERS (*Communicated*): All the advances or discoveries in the use of addition agents have been accomplished by the empirical method. The action of various addition agents with numerous metals is necessary before any theoretical study of the subject should be attempted, such as Dr. Bancroft suggests. Some of this information now being at hand, experiments upon the theoretical principles involved are to be tried next year.

Concerning the difficulty of Mr. Addicks in plating by this method, I can only say that baths of various compositions were used for months and that good results were obtained whenever the composition stated in the paper was approximately used. The pyroligneous acid which he mentions was not tried, hence if he used it in place of aqueous extract of poplar wood or aloes, the conditions of the experiment were not followed.

A paper presented at the Twenty-seventh General Meeting of the American Electrochemical Society, in Philadelphia, at a Joint Session with the American Electroplaters' Society, April 24, 1915, President F. A. Lidbury in the Chair.

CLEANING AND PLATING IN THE SAME SOLUTION.

By Oliver P. Watts.

For a number of years past the electric current has been extensively used for removing grease and dirt from metals after polishing, and as a preliminary to electro-plating. From this use of the electric current for the successive operations of cleaning and plating metals, it was but a short step, in thought at least, to combine the two operations, and perform the cleaning and plating simultaneously in a single solution. Since its inception seven or eight years ago, this process has been steadily increasing in favor among platers, until today it is very widely practiced. Although the combined cleaning and plating solution is sometimes employed to produce the final deposit, its most frequent use is for giving to iron and steel a preliminary coating of copper before nickeling.

For this latter purpose it possesses great advantages over the use of two separate solutions. Not only is there a saving of the time and labor required to transfer the articles from one solution to the other, but any failure to remove the grease is detected while the object is still in the cleaning solution, by the failure of the copper to completely cover the iron.

Since the copper deposit needed for this purpose is very thin, the low current efficiency of the combined cleaning and plating solution is no drawback to its use. When, however, a heavy deposit of metal is desired, it is a different matter. Effective action by an electric cleaner requires an extremely rapid evolution of gas on the object which is being cleaned. But a plating solution in which much gas is evolved at the cathode has of necessity a low current efficiency of metal deposition. On the other hand, the fact that a portion of the current is used in depositing metal makes the cleaning less effective than it would be in the regular electric cleaner. There is therefore a possi-

bility, at least, that the saving in handling consequent upon the use of the combined cleaner and plater may be more than counterbalanced by the loss in time and increased power cost when heavy deposits of metal are desired. A complete solution of this question can only be obtained in commercial establishments, but it is hoped that the author's laboratory experiments, and the limited conclusions which can be drawn from them may prove of interest, and may lead to investigations of this subject by practical platers.

E. G. Lovering,[1] using a combined cleaning and plating solution, claims that he obtains in 20 minutes a deposit of brass 0.002 to 0.003 inch thick, which would require two hours in the regular brass bath. He gives the following as the composition of his solution:

	per liter
½ lb. H. V. W.'s XXX lye	60 g.
2 oz. copper carbonate	15 g.
2 oz. zinc carbonate	15 g.
4 oz. ammonium carbonate	30 g.
4 oz. potassium cyanide	30 g.
1 gallon water	1000 cc.

For a copper solution he uses the same without the zinc carbonate, and claims to obtain a deposit 0.009 inch thick in fifteen minutes, doing in one tank an amount of work which formerly required three tanks. The solutions are used at boiling temperatures.

For comparison with Lovering's solution two ready-prepared compounds were purchased. One of them, for cleaning and depositing copper, will be referred to as *X*, the other, for cleaning and depositing brass, will be known as *Y*.

Copper.

Cleaner "*X*," consisting of a fine white powder, evidently a mixture of caustic soda with other materials, was dissolved in water to form a solution containing 175 g. of solids in 1 liter of water. Although this solution is sold as a cold cleaner and plater, in order to do it justice in comparison with Lovering's solution it was also used hot. Copper electrodes of equal size were used except where the current densities quoted show anode and cathode to have been of unequal areas. Current efficiencies

[1] Metal Industry, 1913, p. 173.

were determined by comparing the weight of copper deposited with that obtained from an Oettel copper coulometer connected in series with the plating solution. Since copper has a valence of one in cyanide solutions, at 100 percent efficiency the weight of copper deposited should be twice that deposited in the coulometer. All current efficiencies for copper have been calculated on this basis.

The results of experiments with cleaner *X* are given in Tables I and II.

TABLE I.

No.	Temperature		Cathode			Time, Min.	Deposit	Anode
	C.	F.	Current Density: Amp. per Sq. dm.	Current Density: Amp. per Sq. ft.	Efficiency			
1	24.5	76	4.	37.3	11.4	60	Fine	Black
2	24.5	76	1.8	16.7	20.6	30	Fine	Black
3	50.	122	2.1	19.5	39.1	30	Good	Black

There was a vigorous evolution of gas at the cathode, but none at the anode, which was soon covered with a black coating, probably cupric oxide. The cathodes consisted of sheet brass coated with grease from the polishing wheels, and received deposits which were perfect in continuity and adherence. A comparison of experiments 1 and 2 shows a considerable increase in efficiency as the result of diminishing the current density, and experiment 3 gives a still greater efficiency as the result of heating the solution. The polarization was 1.3 volts.

TABLE II.

No.	Temp.		Cathode			Anode			
	C.	F.	Current Density: sq. dm.	Current Density: sq. ft.	Efficiency	Current Density: sq. dm.	Current Density: sq. ft.	Efficiency	Anode
4	71	160	7.9	73.5	17.3	5.1	47.4	—3.5	Black
5	70	158	7.9	73.5	16.6	5.1	47.4	—2.4	Black
6	70	158	7.5	70.0	13.8	4.6	43.0	—0.5	Black
7	70	158	1.9	17.7	35.5	1.1	10.2	...	Black
8	70	158	7.0	65.0	14.7	4.6	43.0	4.7	Nearly clean
9	70	158	7.0	65.0	13.3	4.6	43.0	2.7	Clean and bright

Table II shows the effect of the addition of a small amount of potassium cyanide in the hope of dissolving the black film on the anode. The time of deposition was 30 minutes.

The only effect of the addition of cyanide was an improvement in the color and brightness of the deposit. The negative sign before anode efficiencies indicates a gain instead of a loss in weight. In No. 8 an addition of 25 grams per liter of Rochelle salt was made in the hope of inducing corrosion of the anode, and in No. 9 this was increased to 35 grams, with the gratifying result that the black film no longer formed on the anode, although the efficiency of corrosion was still far from satisfactory. It is evident that in order to secure good anode corrosion it will be necessary to lower the current density, add more tartrate, or possibly do both. The previous polarization of 1.3 was unchanged by this addition of the Rochelle salt.

Lovering's solution was next tried. In making this, the zinc carbonate of the formula quoted was replaced by copper carbonate, giving a total of 30 grams per liter of the latter. It was then found necessary to use 70 grams of sodium cyanide instead of 30 grams of potassium cyanide to dissolve the copper carbonate. Tests of this solution are given in Table III.

Table III.

No.	Temperature		Current Density		Efficiency Percent
	C.	F.	Amperes per Sq. dm.	Amperes per Sq. ft.	
10	25	77	3.9	36.3	22.1
11	25	77	1.8	16.7	47.6
12	99	210	3.5	32.5	99.4

At room temperature this solution showed a much higher efficiency of deposition than cleaner *X*, but the anode was entirely black. To improve anode corrosion 20 grams of tartaric acid and 20 c.c. of strong ammonia were added. At the same time it was found necessary to add a small amount of sodium cyanide to completely discharge the blue color of the solution. The result of these changes in the electrolyte and the use of half the former current density is shown in No. 11. In spite of doubling the current density in No. 12, which should lower the

efficiency, other conditions remaining unchanged, elevation of the temperature to gentle boiling has caused a rise in efficiency to practically 100 percent. Under the conditions of No. 12 this solution would not act as an effective cleaner unless a large amount of sodium cyanide were added.

Since the combined cleaner and plater may be considered as only an ordinary cyanide copper solution to which lye has been added, it was considered interesting to compare Lovering's solution with another bath of the same composition except that the lye was left out. A solution was made up of the following composition:

Ammonium carbonate	40 grams
Copper carbonate	36 grams
Sodium cyanide	36 grams
Water	1000 cc.

Tests of this solution (*L*) in comparison with the same to which 50 grams per liter of caustic soda was added (*LA*) are given for 30 minutes of deposition in Table IV.

TABLE IV.

No.	Temperature		Cathode			Anode		
	C.	F.	Current Density		Efficiency	Current Density		Efficiency
			Sq. dm.	Sq. ft.		Sq. dm.	Sq. ft.	
13 *L*	99	210	4.2	39.0	97.4	...	...	...
14 *LA*	99	210	3.8	35.3	96.7	...	...	...
15 *L*	80	176	2.6	24.2	88.6	...	...	...
16 *LA*	80	176	2.9	26.9	85.2	...	...	...
17 *L*	30	86	3.6	33.5	30.6	2.8	26.0	26.7
18 *L*	82	180	3.8	36.3	86.2	3.0	27.9	80.9
19 *LA*	82	180	2.8	26.0	84.9	2.7	25.4	15.7
20 *L*	25	77	2.2	20.4	49.4	3.0	27.9	51.7
21 *L*	25	77	2.5	23.1	34.0	3.0	27.9	34.0

A comparison of 13 and 14 shows that the addition of caustic soda has no effect upon the efficiency of deposition, but the formation of films on the anodes showed the need of more cyanide, and 5 grams per liter of sodium cyanide was added to each solution. This addition is partly responsible for the lower efficiencies of 15 and 16, the other factor in lowering the efficiency being the fall in temperature. On the other hand the

lowering of the current density must have tended in the opposite direction. A comparison of 17 and 18 shows the remarkable effect of temperature upon the current efficiency at each electrode. It has previously been pointed out that elevation of temperature permits the use of unprecedented current densities in nickel plating also.[2] The cause of this greatly stimulating effect of heat upon electrodeposition appears to lie in an increase in the rate of diffusion of dissolved substances with rise of temperature, and the increased circulation of the liquid as a whole, caused by convection currents. To test the effect of artificial circulation upon current efficiency two cells containing the same solution were connected in series so that the same current traversed both, and a stirrer rotated at 1,000 r. p. m. was placed in one cell. The results are shown in 20 and 21, the former containing the stirrer. Since stirring prevents the film of solution in contact with the cathode from becoming depleted in metal it was to be expected that the efficiency of deposition would be increased by stirring. Whenever the current efficiency in a stationary solution is greatly below 100 percent, stirring ought to increase the efficiency, except when the electrolyte contains some corrosive substance such as ferric chloride or an acid, which vigorously attacks the cathode. A comparison of anode and cathode efficiencies for solution *L* shows a very satisfactory state of affairs, as the anode supplies metal at the same rate at which it is deposited. In *LA,* however, the anode was entirely black and corroded so poorly that for long continued use it would be necessary to supply metal by the addition of copper carbonate or cyanide.

It has been stated by Brown and Mathers[3] that the current efficiency of Weil's solution, consisting of copper sulphate, Rochelle salt and caustic soda, is 100 percent at both electrodes for current densities not exceeding 1 ampere per square decimeter. This suggested to the writer the addition of a tartrate for the purpose of increasing the anode corrosion.

To study the effect of a tartrate upon anode corrosion solution *LA* was digested with excess of copper carbonate to re-

[2] Brass World, 1915, p. 34.
[3] J. Phys. Chem., **10**, 51.

move the free cyanide and divided into two portions, to one of which (*LAT*), 60 grams per liter of sodium potassium tartrate was added. Tests of these solutions appear in Table V.

TABLE V.

No.	Temperature		Cathode			Anode		
	C.	F.	Current Density		Efficiency	Current Density		Efficiency
			Sq. dm.	Sq. ft.		Sq. dm.	Sq. ft.	
22 *LA*	71	160	6.6	61.2	33.9	5.1	47.4	3.6
23 *LAT*	71	160	6.0	55.8	35.9	6.1	56.7	55.7
24 *LA*	71	160	6.6	61.2	47.3	5.1	47.1	6.7
25 *LAT*	71	160	6.0	55.8	67.3	6.1	56.7	62.2
26 *LA*	71	160	7.7	71.6	26.8	5.1	47.1	9.4
27 *LAT*	71	160	6.6	61.2	55.1	6.1	56.7	57.1
28 *LA*	99	210	7.7	71.6	79.0	5.1	47.1	39.0
29 *LAT*	100	212	6.6	61.2	97.5	6.1	56.7	100.5
30 *W*	70	158	6.8	63.2	28.4	4.0	37.2	0.3
31 *WCy*	71	160	6.2	57.7	52.1	4.2	39.0	39.7

These tests were made with the two solutions, one without, and one with the addition of the tartrate, connected in series. Nos. 22 and 23 indicated a lack of free cyanide, and 2 grams per liter of sodium cyanide was added to each for tests 24 and 25. For tests 26 to 29, inclusive, the amount of free cyanide was increased to 6 grams per liter. The first addition of free cyanide to *LA* caused an increase in the efficiency of deposition, as well as in anode corrosion; a still further increase in cyanide gave the lessened efficiency at the cathode which had been expected for the first addition. In all tests of *LA* a black coating, probably cupric oxide, formed on the anode, and the corrosion of the anode was absolutely unsatisfactory. The behavior of the anode in *LAT* was in striking contrast to this. As seen in the table its corrosion was closely proportional to deposition at the cathode, and it remained bright and free from any film of oxide or cyanide.

The effect of heating these solutions to boiling was no less striking in 28 and 29 than previously in 12, 13 and 14. In 29 the amount of tartrate had been increased to 110 grams per liter.

To learn more definitely the parts played by the cyanide and

the tartrate in producing the very satisfactory operation of solution *LAT*, Weil's bath, was made up as follows:[4]

Copper sulphate	60 grams
Sodium hydrate (lye)	50 grams
Sodium potassium tartrate	160 grams
Water	1000 cc.

To one portion of this (*WCy*) 30 grams per liter of sodium cyanide was added, just enough to discharge the deep-blue color of the original solution. These two solutions, 30 and 31, were then electrolized in series. The nature of the deposited copper, as well as the current efficiency, indicated that more cyanide was needed in *WCy*, while 30 shows that the tartrate without cyanide does not make a satisfactory solution, for combined cleaning and plating, for it is necessary to use a very high current density in order to cut down the cathode efficiency sufficiently for effective cleaning, and this reduces the anode efficiency nearly to zero.

Two experiments to determine the thickness of metal deposited in a half-hour from the boiling solution *LAT*, at 9 amperes per square decimeter or 84 amperes per square foot, gave 0.0042 in. at a current efficiency of 88.8 percent. At this rate of deposition 1 hour and 4 minutes would have been required for a deposit 0.009 in. thick, such as Lovering obtained in 15 minutes, and a current density of 360 amperes per square foot would have been needed to give this deposit in 15 minutes at the current efficiency of these experiments.

These solutions yielded bright, fine-looking deposits, which gave no indication of stripping from the greasy sheet metal on which the copper was deposited. This must not be taken as an indorsement of the use of these solutions for plating objects with crevices or deep cavities, as no such articles were available for testing.

Cleaner *X* is only suitable for preliminary plating which is to be followed by the deposition of a heavier coating from another solution.

Lovering's solution is capable of doing effective cleaning on flat metal, and will when boiling deposit copper more rapidly than the cold copper sulphate bath, as it permits the use of

[4] J. Phys. Chem., **10**, 51.

higher current densities than the latter. In this connection it should be noted that at 50 percent efficiency for the cyanide bath the deposit of copper equals that by the same current at 100 percent efficiency for the copper sulphate solution.

For effective cleaning it is possible that the current efficiency ought not to be allowed to exceed 50 percent and a high current density must be used.

The hotter the solution the more effective the cleaning, and the higher the current density which may be used without producing a bad deposit.

The proportions of the total current devoted to cleaning and to plating may be controlled by adjustment of the temperature, the amount of copper in the bath, the current density, and the amount of free cyanide present. An increase in the first two, and a diminution of the last two increases the percent of the total current which is devoted to the deposition of metal, and *vice versa.*

The addition of 60 to 75 grams per liter (8 to 10 ounces per gallon) of Rochelle salt or other tartrate to Lovering's bath greatly improves the operation of the solutions.

Brass.

A first attempt to clean metal and deposit brass was made with cleaner *"Y,"* already referred to. A solution containing 175 grams of the powder per liter evolved much gas, and gave only a very thin deposit looking like pure copper at 71° C. and a current density of 6 amperes per square decimeter. As this is supposed to be used cold, it was also tried at 20° C. with current densities of 3 and of 6 amperes per square decimeter. A very thin deposit of red brass was obtained. The solution cleaned the metal, but did not give a satisfactory deposit of brass.

Lovering's brass solution was made up according to the formula previously given, except that more potassium cyanide was needed to secure solution. As the color of the brass deposited from this was not satisfactory, additions of copper and zinc carbonates and sodium cyanide were made, until finally a good color was obtained between 70° and 90° C. The deposits adhered firmly upon sheet metal covered with grease from the

polishing wheels, but thick deposits, equivalent to 15 minutes at 8 amperes per square decimeter, were hard and rather brittle, cracking when the sheet was bent at right angles. No attempt was made to determine current efficiencies. One interesting observation was that the addition of 50 grams per liter of lye to a hot brass plating solution which was depositing brass of an excellent color, caused the color of the deposit to change to that of pure zinc.

The few experiments tried with the brass solution show that brass may be deposited from a combined cleaning and plating solution in a manner similar to copper, but on account of the difficulty of satisfactorily controlling the color of the deposit, the whole matter has been made the subject of a more complete investigation, which is now being carried on in the electrochemical laboratories of the University.

Nickel.

Since the combined cleaning and plating solution for copper is most extensively used as a preliminary to nickeling iron and steel, it was thought that a solution for the simultaneous cleaning and nickeling of iron might be of value to the plating industry. The experiments so far tried for the purpose have failed.

What is needed is an alkaline nickel solution which at or near the boiling point will give a smooth deposit of nickel at a current density of 30 to 50 amperes per square foot, at a current efficiency between 30 and 50 percent.

Naturally cyanide solutions were first tried. A boiling solution containing 70 grams per liter of nickel sulphate in the least amount of potassium cyanide that would dissolve the precipitate gave a bright and adherent deposit of nickel on greasy metal, but the efficiency of deposition proved to be only 0.05 percent. The addition of caustic potash did not improve matters, nor did the substitution of nickel carbonate for the sulphate. The cyanide solution was abandoned, and an attempt was made to hold the nickel in solution by other means. Tartrates prevented the precipitation of nickel by alkalies in cold solutions, but when heated the nickel was precipitated. Experiments are still in progress upon this interesting, but seemingly difficult problem.

The most important result of these experiments is the great

improvement in anode corrosion caused by the addition of a tartrate to the copper solution. Other deductions of less importance are to be found at the close of the section on copper.

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DISCUSSION.

C. G. Schluederberg: In Dr. Watts' paper particular stress is laid on the value of having the solutions hot. In one place, page 149, he says: "The hotter the solution the more effective the cleaning, and the higher the current density which may be used without producing a bad deposit." In talking the other day, with J. O. Jones, Chief Chemist for the Westinghouse Electric and Manufacturing Company, he suggested a possible use of the immersion type electric heater for the purpose of heating these solutions. It seems to me such a heater could be very well applied to this purpose. Most of you probably know that immersion type electric heaters are now used for many and various purposes. They are even used on circuits for making steam in boilers, although that is very expensive unless you have a low rate for current. There is no question but what satisfactory electric heating apparatus could be supplied for the service discussed in this paper.

C. H. Proctor: An occurrence that occurred in my plating department twenty-five years ago will prove that the ideas that Dr. Watts has put forth are correct, but not new.

I think it was in the year 1889 or 1890, while I was employed by the Ansonia Brass and Copper Company at Ansonia, Conn. We were cleaning out some copper tanks. There is a certain amount of sediment which gets in the tanks in use and once or twice a year we cleaned out this sediment. One of my employees was emptying one of the copper tanks and was using a pail to do it. By mistake he took several pails of the copper solution and emptied this in the cleaning solution made of caustic and carbonate of soda. I did not notice this, and nothing was said to me in regard to the addition of the copper solution. When

we finally started up I noticed that in cleaning zinc castings we obtained a reddish coating similar to copper. On making inquiries, I found that some copper solution had been added accidentally to the cleaning solution. I immediately connected up the iron tank with a positive lead, and started to deposit out the copper upon sheets of steel. I noticed at that time that the rusty and greasy surface of the steel was cleansed and I obtained a very good coating of copper, which would prove that Dr. Watts' idea is correct but not new. I used the solution for a certain length of time in this manner, but could not see any economic advantage, so discarded its use.

To hold copper in a cyanide solution you must have free cyanide. In heating the solution to 212° F. (100° C.) and removing the grease and organic matter the cyanide decomposes quite rapidly and must be renewed quite often, which proved that the proposition was too costly for use, and I finally discarded the idea of using a combined cleaner and plater. Probably for small articles it may be an advantage. If you could deposit copper from carbonate of sodium or caustic hydrate, we should not have any use for cyanides. Three years ago I was in a plating department in Chicago and later in Cleveland, and cleaning and plating was being utilized there, so it is not a new process.

George B. Hogaboom: Dr. Watts said he did not get successful brass deposition. Since the paper was published, I have had a little experience. We have a mechanical plater, with a 350-gallon electric cleaner, and have a foreigner who can not talk English, operating it. He went to the storeroom, as is his practice every morning, to get a certain amount of causticised ash, and instead got forty-five pounds of zinc carbonate and put it into the cleaner. To see what would happen I put in two pounds of cyanide of sodium; the cyanide present dissolved enough copper from the plating racks, which held the work, to combine with the zinc to give a beautiful brass deposit.

S. D. Benoliel: Some of the speakers have referred to this method as being impractical. This is certainly true because the method has but very limited applications. In cleaning work before plating, there are a large variety of metals to be cleaned,

such as iron, zinc, German silver, brass, etc. Again, the nature of the material to be removed plays an important part. These articles vary to a great extent, and may be composed of such materials as mineral oils, lubricating compounds, vaseline buffing compositions, which may be made up with paraffin, stearic acid, etc., all of which goes to make the problem more or less complicated.

FRANCIS C. FRARY: I would suggest that you use instead of the cyanide, to hold the copper in solution, some form of invert sugar, cheap glucose, or even cane molasses (preferably first warmed up a little with some acid) because it is well known that these invert sugars will hold copper in alkaline solution as well as the expensive tartaric acid compound. If the process is worth using for any purpose, you might be able to make a saving by this substitution.

GEORGE B. HOGABOOM: In reply to Dr. Frary's statement, I would say that we are making certain solutions containing glucose, corn syrup, 58 percent, 42° Baume, manufactured by the Corn Products Company. In removing the work from the solution containing a substance such as you speak of, and putting it into cold water, the work discolors very rapidly, and it is necessary to pass it through a bath of cyanide to clarify the deposit.

FRANCIS C. FRARY: Did you try the cheapest grade of dextrose sugar instead of glucose?

GEORGE B. HOGABOOM: We used it in zinc plating. If there is any appreciable amount in the solution, it discolors the work and requires cyanide to clarify it.

MR. WATTS (*Communicated*): Concerning the reputed failure of the combined cleaning and plating solution from the economic standpoint, due to excessive consumption of cyanide by the hot solution, I can give no evidence, as my experiments were of too brief duration to determine this point. Although, as previously stated, cleaning is most effective in boiling solutions, excellent results have been obtained at temperatures as low as 60° C. At this lower temperature and with the less vigorous agitation which accompanies it, it is possible that the destruction

of cyanide may be sufficiently lessened to permit of the economical use of the combined cleaning and plating bath.

Mr. Benoliel's contention that the method is of very limited application because of the great variety of metals to be cleaned and the many different kinds of grease to be removed in practical plating is incorrect. No other method of cleaning in use today is capable of such general application to all kinds of metals for the removal of every variety of grease as is the combined cleaning and plating solution.

A paper presented at the Twenty-seventh General Meeting of the American Electrochemical Society, at Atlantic City, N. J., April 23, 1915, President F. A. Lidbury in the Chair.

DEPOLARIZATION IN LE CLANCHÉ CELLS.

By M. de Kay Thompson and Ernest C. Crocker.

In the LeClanché cell the positive electrode consists of carbon in contact with manganese dioxide. The dioxide acts as the depolarizer, but does not depolarize completely, as is shown by the gradual decrease in the current and voltage on closed circuit. LeClanché recommended that the manganese dioxide should be mixt with carbon and that both should be coarse in size.[1] This point was investigated, in 1873, by Beetz, who found that the best depolarization is obtained with the carbon "coarse" and the manganese dioxide "fine".[2] The exact sizes were not given, nor was there any study made of the best proportions in which to mix the carbon and dioxide. There has, apparently, been nothing publisht on this subject since the work of Beetz, altho it has doubtless been studied by the manufacturers of LeClanché cells.

LeClanché cells, in various forms, are extensively used at the present time, especially as dry cells. About fifty million a year are manufactured in the United States alone. Wet cells are also made in smaller quantities. In the wet cell the positive pole is either a plate made of carbon, manganese dioxide and a binder, or a mixture of particles of carbon and manganese dioxide about the size of peas placed inside the carbon electrode or fastened outside of it in cloth sacks, as in the large size *Samson* cell. In dry cells the depolarizing mixture is much finer than in the Samson cell.

On account of the incompleteness of the previously publisht work, and on account of the fact that the depolarizing mixture is made in such different sizes in different makes of LeClanché cells now in use, it was decided to make a study of the compara-

[1] Wiedemann, Die Lehre von der Elektrizität, I, 850 (1893).
[2] *Ibid.*, p. 853.

tive efficiency of depolarizing mixtures of carbon and manganese dioxide, when the sizes of the particles and the relative amounts of the substances present in the mixture were varied. This was the primary object of the following investigation, altho in the course of the work the mechanism of polarization was also studied, as will be seen below.

Determination of the Best Sizes of Carbon and Pyrolusite Particles.

The experiments for determining the best sizes of carbon and pyrolusite in the depolarizer were carried out in cylindrical bat-

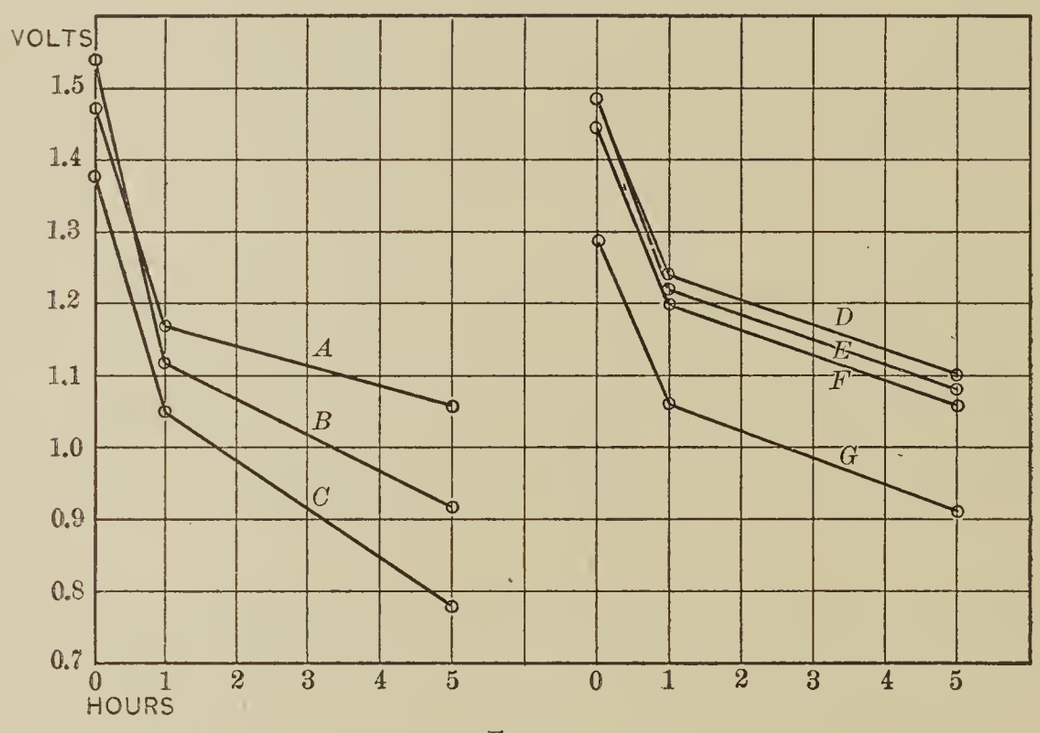


FIG. 1.

tery jars 13 cm. high and 11 cm. in diameter. The anodes were sheet-zinc cylinders 10 cm. high and 9 cm. inside diameter, made for *Samson* batteries. The electrolyte was in all cases a 15 per-cent solution of ammonium chloride to which was added varying amounts of zinc chloride. The cathodes were carbons taken from *Columbia* dry cells. These carbons were thoroly cleaned and placed in porous Pukal clay cups 14 cm. high and 5.8 cm. outside diameter. The depolarizing mixture was then packt, dry, around the carbon by tamping with as much pressure as was considered safe for the porous cups.

The method of testing was to connect four cells in series,

in each of which only a single factor was varied, and to pass thru them a constant current from an external source, measuring at definite intervals the voltage of the cathode against a normal calomel electrode. The circuit was opened momentarily during the measurement to prevent the drop in voltage in the cell from affecting the results. The factors thus studied were (1) size of carbon and pyrolusite particles, (2) relative amounts of carbon and pyrolusite, and (3) purity of pyrolusite.

The carbon used to mix with the pyrolusite consisted of equal parts of gas carbon and Acheson graphite. The pyrolusite used in all experiments unless otherwise stated was the 95 percent

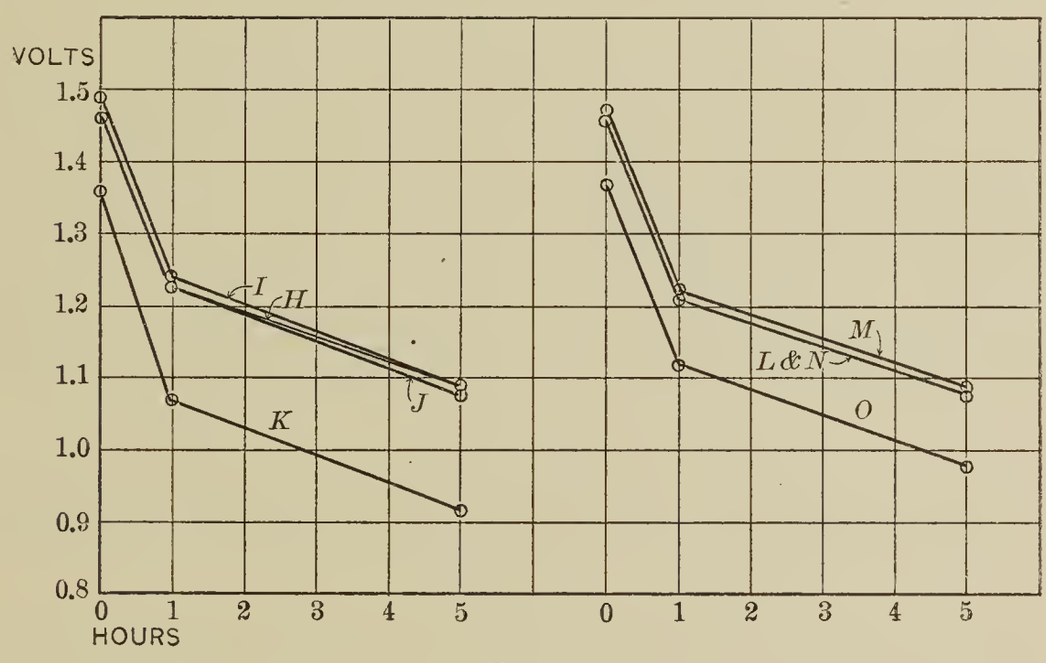


FIG. 2.

natural product, obtained from Eimer and Amend. The following table gives the analysis of the pyrolusites used, after crushing and sizing.

Grade	Size	Percent MnO_2
95 percent	16/30	97.4
95 percent	60/120	94.0
85 percent	60/120	90.7
Artificial, fine	———	68.5

In giving sizes of particles, the notation 16/30 means that the particles passed thru a sieve with meshes 1/16 inch square and were held by a sieve with meshes 1/30 inch square.

The combinations of sizes tested are shown in the accom-

panying table, in which A means that the combination was tried in preliminary runs only, where it was found too poor to warrant further study; while B means that the combination was further tested in two similar cells simultaneously.

Size of Pyrolusite	Size of Carbon				
	4/10	10/20	20/40	40/80	Thru 80
8/ 16	B	B	B	A	. . . . .
16/ 30	B	B	B	A	. . . . .
30/ 60	A	A	B	B	. .
60/120	. . . . .	A	A	B	B
Thru 120	A	A	A	A	. . . . .

The mixture for the tests on the sizes of particles in the depolarizer, was 90 grams of carbon thoroly mixt with 90 grams of pyrolusite. Not more than one-third of the theoretical depolarizing power of the pyrolusite was used up in any run.

The results of the preliminary tests are given in Table I and Figs. 1 and 2. The current was kept constant at 0.25 ampere, and the solution contained 15 percent of ammonium chloride.

TABLE I.

Effect on Polarization of the Sizes of Pyrolusite and Carbon Particles. Preliminary Tests.

Curve No.	Size of Particles		Open Circuit Voltages		
	Carbon	MnO_2	Initial	1 Hour	5 Hours
A	4/10	8/16	1.48	1.17	1.06
B	4/10	30/60	1.54	1.12	0.92
C	4/10	Thru 120	1.38	1.05	0.78
D	10/20	8/16	1.49	1.24	1.10
E	10/20	16/30	1.49	1.22	1.08
F	10/20	30/60	1.45	1.20	1.06
G	10/20	Thru 120	1.29	1.06	0.91
H	20/40	8/16	1.47	1.23	1.09
I	20/40	16/30	1.49	1.24	1.09
J	20/40	30/60	1.46	1.23	1.08
K	20/40	Thru 120	1.36	1.07	0.93
L	40/80	8/16	1.46	1.21	1.08
M	40/80	16/30	1.47	1.22	1.09
N	40/80	30/60	1.44	1.21	1.08
O	40/80	Thru 120	1.37	1.12	0.98

These results show that the finest pyrolusite gave the poorest depolarization, (curves C, G, K, and O). Where the pyrolusite and carbon particles were of approximately the same size the depolarization was best, and became poorer as the sizes differed more and more from each other. This is shown in curves A to G. The curves H, I, J, L, M, N, are all approximately the same, as there was no great difference in the sizes of the particles in these experiments.

Table II and Figs. 3 and 4 contain the results of further study of the more favorable mixtures. The results are the average values obtained from two similar cells. The cells were made up in the same way as those used in the preliminary runs, and were allowed to stand 12 hours before beginning the run. One quarter of an ampere was passed for an hour, taking open circuit voltages with the normal electrode at the times 0, 15, 30, and 60 minutes. The current was then increased to 0.50 ampere, and the open circuit voltage taken at the end of 15 minutes. The cells then stood on open circuit for 15 minutes. After this rest, 1.5 amperes were passed for 15 minutes, and the open circuit voltage read at the end of this time. The electrolyte was a 15 percent solution of ammonium chloride to which 0.7 percent zinc chloride was added to give steadiness to the single-potential of the zinc electrode.

TABLE II.

Effect of Size of Carbon and Pyrolusite on Depolarization. Final Tests.

No.	Size of		Open Circuit Voltage					
			0.25 Ampere				0.5 Amp.	1.5 Amp.
	Carbon	MnO_2	0 Min.	15 Min.	30 Min.	60 Min.	15 Min.	15 Min.
1	10/20	8/16	1.56	1.41	1.35	1.28	1.21	1.01
2	10/20	16/30	1.57	1.41	1.35	1.27	1 18	0.92
3	4/10	8/16	1.53	1.37	1.31	1.25	1.16	0.87
4	4/10	16/30	1.55	1.31	1.23	1.16	1.01	0.12
5	40/80	30/60	1.53	1.42	1.37	1.29	1.24	1.11
6	20/40	16/30	1.55	1.42	1.36	1.28	1.20	1.07
7	20/40	8/16	1.54	1.39	1.34	1.27	1.19	1.05
8	20/40	30/60	1.53	1.39	1.34	1.27	1.19	1.04
9	40/80	60/120	1.48	1.37	1.32	1.25	1.17	1.04
10	Thru 80	60/120	1.46	1.38	1.34	1.29	1.23	1.10

The results in Table II, and curves 3 and 4, confirm the results of the preliminary tests. The depolarization produced by the coarser sizes, as is shown in curves 3 and 4, was less favorable than that due to the finer sizes shown in curves 1 and 2.

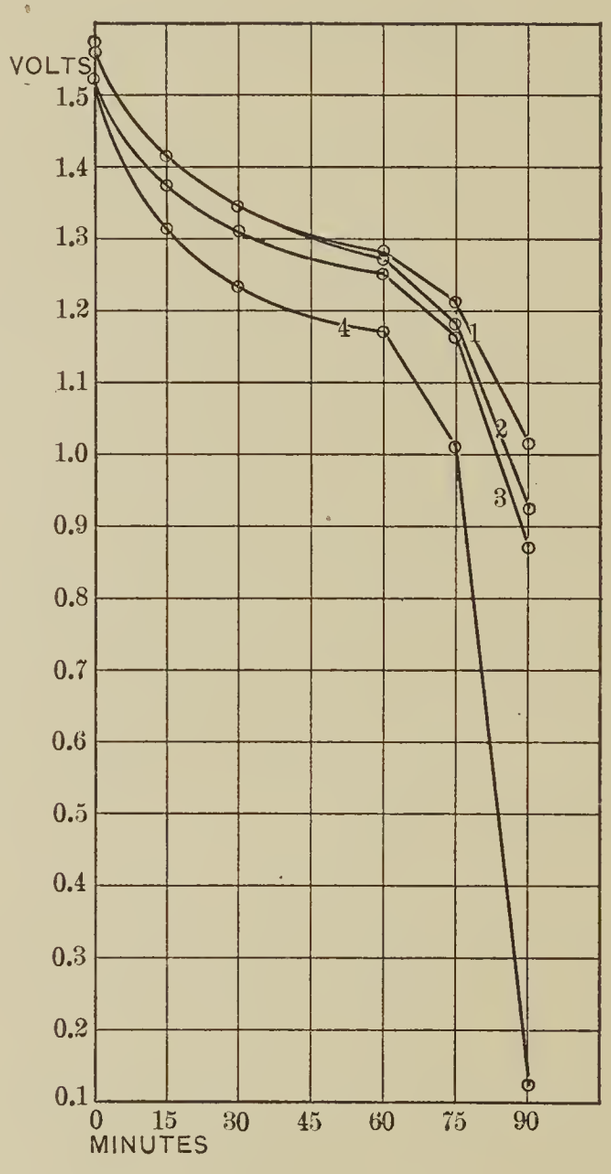


FIG. 3.

The difference between curves 2 and 4 is only that the size of the carbon has been changed from 10/20 in curve 2 to 4/10 in curve 4. In curves 1 and 2 the size of carbon is the same, but the pyrolusite is 8/16 in curve 1 and 16/30 in curve 2, showing a falling off in the depolarization on changing the size of the pyrolusite to a different size from that of the carbon. The

particles of pyrolusite and carbon should therefore be of the same size.

On grinding the pyrolusite and sizing, the largest and smallest sizes differed in purity by 2.4 percent, but the difference in purity in the sizes 8/16 and 16/30 was only a small part of this and therefore not enough to account for the differences in polarization observed. The difference must therefore be due to the difference in the size of the pyrolusite.

As to the absolute sizes of the particles of the depolarizing mixture, there seems to be very little choice between the sizes tested in these experiments. The fact that the curves D, E, F,

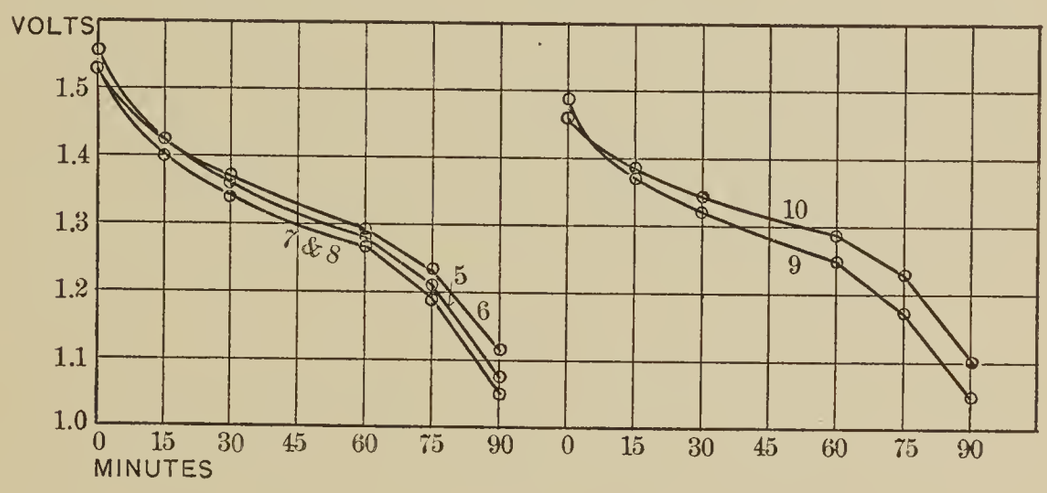


FIG. 4.

H, I, J, L, M, and N are all above A indicate that the particles should be smaller in diameter than 1/10 inch (0.25 cm.). Also, the poor depolarization with pyrolusite smaller than 1/120 inch (or 0.02 cm.) diameter indicates the lower limit. The particles of the depolarizer should accordingly be less than 1/10 inch and larger than 1/120 inch in diameter.

Table III and Fig. 5 show the effect of the purity of the pyrolusite used for depolarization. The electrolyte contained 15 percent ammonium chloride and 0.7 percent zinc chloride, except in curve 8, when it contained about 4 percent zinc chloride. The experiments were carried out in the same way as those given in Table II.

TABLE III.

The Effect of Purity of Pyrolusite on Depolarization.

No.	Size of		Purity of MnO_2 Percent	Open Circuit Voltage					
				0.25 Ampere				0.5 Amp.	1.5 Amp.
	Carbon	MnO_2		0 Min.	15 Min.	30 Min.	60 Min.	15 Min.	15 Min.
1	40/80	60/120	94	1.48	1.37	1.32	1.25	1.17	1.04
2	40/80	60/120	93	1.45	1.33	1.28	1.23	1.17	1.04
3	40/80	60/120	90	1.47	1.29	1.24	1.18	1.09	0.91
4	4/10	Absent	—	1.38	0.53	0.36	0.11	...	...

These results show that a change in the purity of the pyrolusite of 4 percent has a decided effect on the depolarization.

Table IV and Fig. 6 show the effect on depolarization of varying the relative amounts of carbon and pyrolusite in the depolarizing mixture. The electrolyte contained 15 percent ammonium chloride and 5 percent zinc chloride. The pyrolusite was the 95 percent grade. The method of carrying out the experiment remained the same.

TABLE IV.

Effect of Relative Amounts of Carbon and Pyrolusite on Depolarization.

No.	Percent MnO_2	Sizes		Open Circuit Voltage					
				0.25 Ampere				0.5Amp.	1.5Amp.
		MnO_2	C	0 Min.	15 Min.	30 Min.	60 Min.	15 Min.	15 Min.
1	58	16/30	16/30	1.56	1.45	1.40	1.33	1.27	1.07
2	42	16/30	16/30	1.52	1.40	1.35	1.30	1.23	0.96
3	31	16/30	16/30	1.50	1.37	1.33	1.28	1.22	1.01
4	69	16/30	16/30	1.54	1.36	1.32	1.27	1.14	0.04
5	55	30/60	30/60	1.55	1.45	1.40	1.34	1.27	1.14
6	60	16/30	12/20	1.58	1.45	1.40	1.34	1.26	1.03
7	50	16/30	12/20	1.54	1.42	1.37	1.31	1.24	1.00
8	55	16/30	12/20	1.56	1.42	1.37	1.32	1.23	0.95

Experiments 1 to 4 are comparable because the size of the depolarizer is the same. Of these the 58 percent mixture gave the best depolarization. In experiments 6 to 8 the 60 percent mixture gave the best depolarization. These results indicate

that the depolarizer should contain approximately 60 percent of manganese dioxide.

The Cause of Polarization in LeClanché Cells.

Manganese dioxide is considered a weak depolarizer because when a continuous current of appreciable magnitude is taken from a LeClanché cell there is a steady fall of voltage. It is

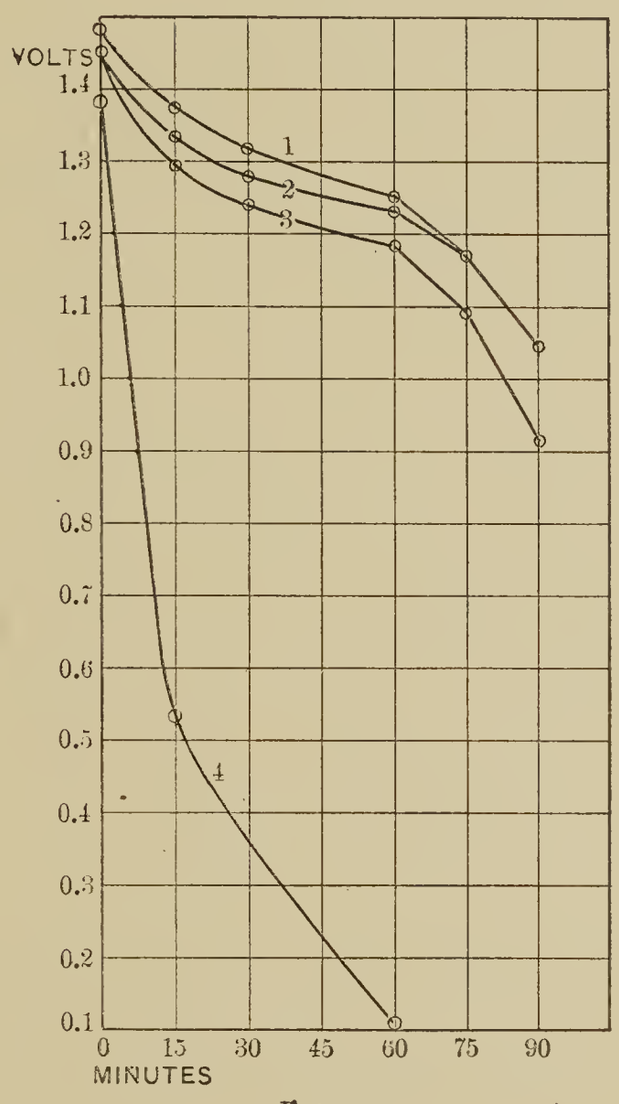


FIG. 5.

natural to assume that at least a part of the polarization is due to the incomplete oxidation of the hydrogen, which may be supposed to form on the decomposition of the ammonium radical and its subsequent splitting up, represented in the equation

$$2NH_4 = 2NH_3 + H_2$$

It has been found, however, that even with the highest current densities there is no liberation of hydrogen. This was shown

by using a large lump of pyrolusite as the positive electrode in a small cell. (Contact was made by wrapping the end not immersed in the ammonium chloride solution with a copper wire.) With a zinc anode this cell gave on open circuit 1.53 volts. A current of 0.25 ampere was passed for 12 minutes without any evolution of hydrogen. The surface of the pyrolusite was 5

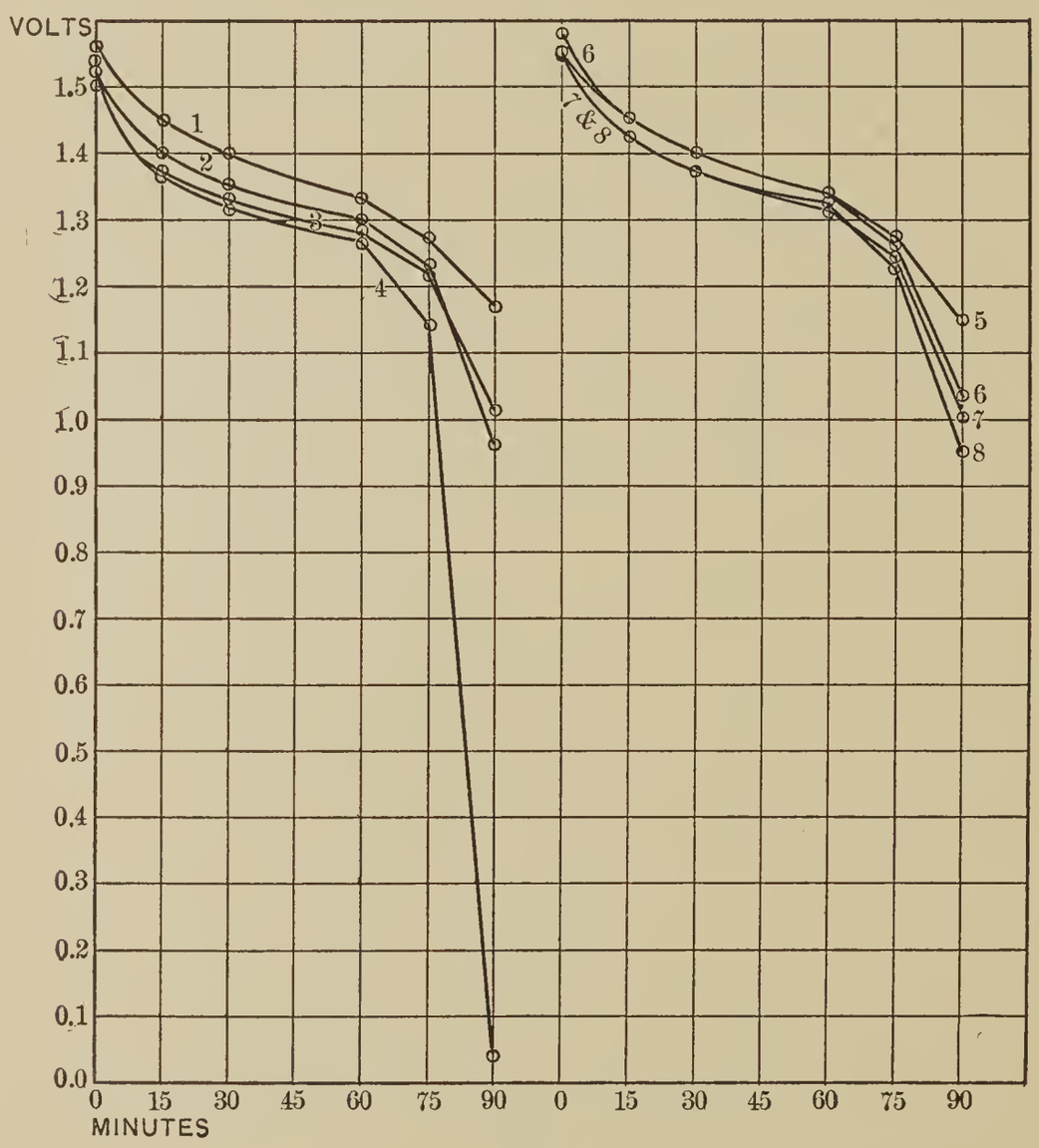


FIG. 6.

sq. cm. in area so that the current density had the very high value of 0.05 ampere per sq. centimeter. Furthermore, none of the cells showed any trace of gas bubbles during the tests. It is therefore evident that pyrolusite oxidizes one atom of hydrogen in each ammonium radical liberated on its surface, or on the surface of carbon in intimate contact with it, with 100 percent efficiency, and that no molecular hydrogen is formed. Whether

this oxidation takes place while the hydrogen is still in the ammonium radical or while in the nascent state is an open question.

The cause of polarization in the LeClanché cell must therefore be the other cathode product, the ammonia, or, as is shown below, by the hydroxyl ions resulting from the ammonia. If this be the case, the removal of the ammonia as rapidly as it is produced should prevent polarization, except in so far as it is the result of the using up of the pyrolusite. That ammonia reduces the potential of the positive electrode (or causes polarization) is shown in Table V, in which are given the voltages of cells of the type

$$Hg \mid HgCl, KCl \mid NH_4Cl, NH_4OH \mid MnO_2, C$$

(The current tends to flow in the cell from left to right.)

TABLE V.

Effect of Different Concentrations of Ammonia and Ammonium Chloride on the Potential of the Positive Electrode.

Concentration of NH_4Cl Percent	Concentration of Ammonia. Percent		
	0	0.5	5
0.1	0.48 volt	0.37 volt	0.22 volt
1.0	0.48 "	0.41 "	0.35 "
10.	0.48 "	0.44 "	0.38 "
Saturated	0.48 "	0.44 "	0.39 "

The following methods of reducing the hydroxyl-ion concentration may be considered:

(1) Increase of the NH_4^+ ion concentration, thereby driving back the dissociation of the ammonia;

(2) Addition of H^+ ions;

(3) Addition of a salt of a weaker base than ammonia; the ammonia would tend to unite with the acid and liberate the weaker base;

(4) Addition of a neutral substance to combine with ammonia (NH_3);

(5) Addition of a neutral substance to destroy the ammonia.

Table V shows that for a given concentration of ammonium chloride an increase in the ammonia concentration lowers the voltage; also that for a constant ammonia concentration an increase in the ammonium chloride raises the voltage as indicated under (1).

(2) The addition of hydrogen ions is impracticable because of the solvent action on the zinc electrode. The salts which ammonia forms with such weak acids as boric acid, acid phosphates, and acids of the acetic series, are hydrolyzed to such a large extent that the alkalinity is only partly removed. This accounts for the unsatisfactory results which were obtained with these acids.

(3) The salts of any base weaker than ammonia hydrolyze to such an extent that the hydrogen-ion concentration becomes too high and the zinc becomes attacked.

(4) Zinc chloride combines with a considerable amount of ammonia, and it was found well suited for reducing the hydroxyl-ion concentration.

(5) Formaldehyde was tried for the purpose of destroying the ammonia, but it attacked the ammonium chloride setting free hydrochloric acid, which in turn attacked the zinc.

The effect of alkalinity and acidity is further shown in Table VI. The cells whose electromotive forces are given in the table were made up as follows:

$$Hg \mid HgCl, N\ KCl \mid Sat.KCl \mid Electrolyte \mid MnO_2, C$$

(The current flows from left to right in the cells.)

TABLE VI.

Potential of Manganese Dioxide Electrode in Different Solutions.

Solution	Normality	Voltage		
		10 Min.	30 Min.	60 Min.
KCl	1.0	0.482	0.482	0.482
NaOH	1.0	0.049	0.049	0.053
NaOH	0.01	0.310	0.307	0.313
H_2SO_4	2.0	0.955	0.958	0.963
H_2SO_4	0.02	0.757	0.765	0.775

That the manganese dioxide may be considered an oxygen electrode is suggested by the data in Table VI. If P is the electrolytic solution pressure of oxygen corresponding to the gaseous pressure of the equilibrium $3\ MnO_2 = Mn_3O_4 + O_2$ and p is the osmotic pressure of the oxygen ions, the potential of the oxygen electrode is $e = RT/2\ log_e\ P/p$.

A cell made of two such electrodes, one in a solution with oxygen ions of concentration C_1 gram ions per liter, the other with C_2 gram ions per liter, would have the electromotive force $e_1 = RT/2\ log_e\ C_1/C_2$. The concentration of oxygen ions of a solution can be shown by the mass action law to be inversely as the square of the hydrogen ions: (C_1/C_2) oxygen $= (C_2/C_1)^2$ hydrogen. Therefore the above value of $e_1 = RT\ log_e\ (C_2/C_1)$ hydrogen. In normal sodium hydrate, the hydrogen ion concentration is 0.97×10^{-14}, and in $2N$ sulfuric acid it is approximately 0.35 (gram ions per liter).[3]

The electromotive force of a cell made up of two oxygen electrodes, one dipping into $2N\ H_2SO_4$ the other in $1N$ NaOH would therefore be

$$e = RT\ log_e\ 35/97 \times 10^{-14} = .058 \times 13.6 = 0.79 \text{ volt.}$$

This agrees approximately with 0.90 in Table VI.

The manganese dioxide electrode has been studied by Tower[4] and Smith[5]. Tower's formula for the potential of a manganese

[3] Since $H^+ \times OH^- = (0.84 \times 10^{-7})^2$ (LeBlanc, p. 194, 1911) and OH^- in N NaOH is 0.73 gm. ion per liter.

The concentration of hydrogen ions in $2N$ sulfuric acid may be calculated from the electromotive forces of the following cells, taken from the *Abhandlungen der Deutschen Bunsen Gesellschaft, No. 5.* The electromotive force is directed from left to right within the cell as they are written.

From the cells:

Pt | H_2, $2N H_2SO_4$ | $1N H_2SO_4$, sol. Hg_2SO_4 | Hg = 0.692
Hg | Hg_2Cl_2, NKCl | $1N H_2SO_4$, Hg_2SO_4 | Hg = 0.375
Hg | Hg_2Cl_2, NKCl | $0.1N$KCl, Hg_2Cl_2 | Hg = 0.051
Pt | H_2, NHCl | KCl sat. | $0.1N$KCl, Hg_2Cl_2 | Hg = 0.355

and the dissociation of NHCl, the concentration of hydrogen ions in $2N H_2SO_4$ is 0.39 gm. ion per liter.

From the cells:

Pt | H_2, $0.1N$HCl | $0.1N$KCl, Hg_2Cl_2 | Hg = 0.400 corrected for the liquid-liquid junction.
Hg | Hg_2Cl_2, NKCl | $0.1N$KCl, Hg_2Cl_2 | Hg = 0.051
Pt | H_2, $2N H_2SO_4$ | $1N H_2SO_4$, Hg_2SO_4 | Hg = 0.692
Hg | Hg_2Cl_2, NKCl | $1N H_2SO_4$, Hg_2SO_4 | Hg = 0.375

the concentration of hydrogen ions in $2N H_2SO_4$ is 0.32 gram ion per liter. The average is 0.35.

[4] Zeit. f. Phys. Chem., **18**, 35 (1895); **32**, 568 (1900).

[5] Zeit. f. Phys. Chem., **21**, 93 (1896)

dioxide electrode dipping into a solution containing a definite concentration of manganese ions is

$$e = \frac{RT}{2F} \log_e \frac{[(Mn^+)\ (OH^-)^4]'}{[(Mn^+)\ (OH^-)^4]''}$$

and is based on the reaction $MnO_2 + 2H_2O = Mn(OH)_4$. The measurements however, do not agree exactly with this formula in acid solutions, nor do his measurements agree with the formula proposed above. In alkaline solutions saturated with $Mn(OH)_2$ Tower's formula reduces to the one proposed above, since $Mn^+ \times (OH^-)^2 =$ constant, and in this case his measurements agree with the formula. It therefore appears that only when the solution is saturated with manganous hydroxide can its potential be calculated on the assumption that it is an oxygen electrode.

Summary of Results.

1. The carbon and pyrolusite particles should have the same size, and this should be such as to allow the particles to pass thru openings 1/10 inch (0.25 cm.) square and not to pass thru openings 1/120 inch (0.02 cm.) square.

2. The purity of the pyrolusite affects the depolarization materially.

3. The mixture of carbon and pyrolusite should contain 55 to 60 percent pyrolusite.

4. Polarization by hydrogen is completely prevented by the dioxide; the remaining polarization is that due to ammonia. This may be largely overcome by the addition of zinc chloride to the solution.

Massachusetts Institute of Technology,
Boston, June, 1914.

DISCUSSION.

C. F. Burgess (*Communicated, read by Mr. Hinckley*): It is a peculiar fact that one type of primary cell has had a great deal of attention in scientific laboratories while another type of far greater importance has been practically neglected. There is an extensive literature relating to "standard cells" and some notable work has been done in the development of electrochemical standards of electromotive force. While hundreds of thousands of "dry cells" are used to one of the standard cells, and while they are playing an important part in everyday life, there is only a meager literature relating to the scientific problems of dry cell construction.

The authors of this paper have taken an important step toward remedying this condition. There are various problems which the manufacturers of dry cells do not yet understand. One of the features of the construction which has not been generally understood is the necessity of employing zinc chloride as a constituent of the electrolyte. The explanation for it given by this paper is undoubtedly correct.

The conclusion is stated that carbon and pyrolusite particles should be of the same size, and not finer than 1/120 inch (0.02 cm.). While this conclusion might be drawn from the particular method of construction used, it may not apply under other methods of construction. The high capacity flash-light cells on the market use finer materials than this, and apparently with great advantage. One of the difficulties of conducting comparative tests is the large number of variables which must be considered. The pressure of tamping is a most important factor. The amount of moisture is another one. The small amounts of certain impurities may dictate one method of construction with one grade of material and another method with another grade, to develop the best results.

Referring to Table I, it would be of interest to have an explanation as to why the initial electromotive force of the cell is so much less with the very fine material than with the coarse. Why does the electromotive force vary with the size of particles, assuming equivalent chemical composition?

It has been the experience in the manufacture of dry cells

that the percentage of MnO_2, through a narrow range of limits, is not of great importance, as is, indeed, shown in Tables III and IV. Through the difficulty of getting the standard grade of manganese under existing war conditions, much work has been done on the use of pyrolusite from various other sources. This brings out the important fact that there are characteristics of the pyrolusite other than the percentage of MnO_2 that control the capacity of a cell. Whether these differences are due only to chemical composition or to physical properties, or to both, is not perfectly clear.

N. K. Chaney (*Communicated, read by Mr. Mott*): In Table VI the various potentials of the manganese dioxide electrode are given for certain acid, alkaline, and neutral salt electrolytes.

From a twice normal H_2SO_4 solution to a once normal NaOH solution the drop in potential of the manganese electrode is from 0.95 to 0.05 volt. Would the writers refer to this drop in voltage as "sodium hydroxid," or "hydroxyl" *polarization*? If so, all potential variations due to the characteristics of different electrolytes are *polarization* phenomena. If this definition be not accepted, then is it permissible to refer to the change in the potential of the manganese electrode with increase of free ammonia concentration as a *polarization* effect?

The question is whether the term polarization should be restricted to changes supposed to occur in or on the surface of the electrode, or whether concentration differences and other changes arising in the character of the electrolyte are also understood as included in the use of the term.

The existence of hydrogen polarization of the manganese electrode is denied upon the basis of results obtained with a current density of 0.05 ampere per square centimeter upon a solid manganese dioxide electrode.

It would be of interest to have a further description of this manganese, as the standard Caucasian manganese has much too high a resistance to permit drains of this density to pass, and the writer has been unable to duplicate this experiment with any material in his possession.

Jos. W. Richards: Speaking from the standpoint of the mineralogist, natural pyrolusite is a very variable material.

Pyrolusite and its congener wad are about the most variable minerals in composition in the whole mineralogical field; and, therefore, nothing very definite can be attained in this line unless some one starts first with practically the purest manganese dioxide obtainable and then afterwards gets results with various known mixtures of impure material.

FRANCIS C. FRARY: I would suggest that the rate of the depolarizing action of the manganese dioxide is a question of its solubility in the electrolyte, more than of anything else, and that the probable effect of adding zinc chloride to the material would eventually be found to be evidence that the depolarization produced by the manganese dioxide is conditioned by the rate of solution of the manganese dioxide and its concentration around the carbon electrode. The obvious depolarization reaction is that of the manganese dioxide going into solution and being reduced in solution, and would be similar to the electrode effects which we have in the storage battery.

W. R. WHITNEY: It is unfortunate that professors like these at the Massachusetts Institute of Technology have to do just this kind of work, and I want to point out why they probably have to do it. In the first place, there is the student, who wants to work in something practical. In the second place, there is not enough encouragement in this country for men in their position to do the pure chemical research. If they started to dissolve and reprecipitate the manganese dioxide, to get pure materials, they would find they were introducing an expense which the commercial attitude seems, I think erroneously, to consider unwarranted.

H. K. HITCHCOCK: Quite recently a member of the faculty of a prominent school came to me and said that one of his graduate students wanted to make a research on the physical properties of glasses having certain variables, and wanted to know if we could give him any assistance in that matter. I told him that we would be glad to furnish him with a furnace and with all the materials required, and especially with the proper kind of pot or crucible, the having of which would be very essential to success; that it would take him a long while to get pots that would be suitable to make glass in and get good

results, but that we would be glad to make them for him, and in fact, give him everything he needed and point out the most fruitful field of research into which he could go. We went over in detail the various points that he would have to take care of, pointing out the necessity of a uniform heat treatment for each kind of batch which he used. The result was that when we got through telling him the immense number of variables which might influence his work before he finished, he never came for the crucibles and we are still waiting for him.

I cite this to show that the average corporation is very glad to get the practical co-operation of a Society like this, and will do its share towards furnishing the means to prosecute that work, while the results obtained would be open to everybody.

W. S. Franklin: I think the share of the corporation in that thing is the whole business. I think they should be not only willing to furnish the pots and the materials and the furnace, but they should also hire a man to do the work and keep him at it five or ten years until he can get something out of such an enormous mass of variables.

I think the time is coming when our industries have got to do that sort of thing to an extent enormously in excess of what they are doing now with the single exception, perhaps, of the General Electric Company. I tell you, gentlemen, that practical men are making a mistake when they have as their ideal the college or university as the place where research, pure research even, can be done to the best advantage. The time is coming in this country when the chief research work will be done in connection with industrial establishments. I have come to believe even that our industrial establishments are our best schools, and I certainly believe that our industrial establishments should be our best research institutions.

H. K. Hitchcock: In answer to Dr. Franklin, I would say we have had a corps of men at work on the question of the pot itself for several years, and we offered to the Technical School pots which embodied all of that experience, so that they would not have to contend with unsuitable apparatus. We also offered to pick out for them the simplest and most practical problem which they could tackle, which would be of actual

commercial value to the world at large, not expecting them to cover the whole field. We said, "Here is a little field that you can cover, and you can just work along on this particular field; or here are a dozen other fields that we will be glad to get data on. We are not interested in lead glass. We do not manufacture it. We are not now interested in optical glass, as we do not manufacture that, either. But there are people who are interested in them and from what we have already done we know that there is a fertile field for you to work in, and we will give you all of the assistance we possibly can. Come up to our laboratories, and we will show you how we are working out our problems, and we will give you any information that we possibly can that will assist you in working out yours."

I make these remarks simply to point out that the average manufacturer is not unwilling to co-operate with any school which wants to attack practical problems, and will give them the benefit of what he has done in so far as it will help them in getting a proper method of attack and assure a good start.

M. DE K. THOMPSON (*Communicated*): In reply to Mr. Chaney's discussion of the above paper, I would say that my understanding of *polarization* is that it means the back electromotive force due to the passage of an electric current. Thus, if a current passes through a zinc sulphate solution by means of zinc electrodes, concentration changes take place at the electrodes that produce an electromotive force in the reverse direction. If the same concentration changes were produced by some other means than the electric current, the same electromotive force would result, but it could not be called polarization.

The manganese dioxide was in the form of lumps; its source is not known.

A paper presented at the Twenty-seventh General Meeting of the American Electrochemical Society, at Atlantic City, N. J., April 23, 1915, President F. A. Lidbury in the Chair.

NEUTRALIZATION OF ADSORBED IONS.

By Wilder D. Bancroft.

Any substance may be brought into a state of colloidal solution provided we make the particles of that phase so small that the Brownian movements will keep the particles suspended, and provided we prevent agglomeration of the particles by a suitable surface film.[1] Coalescence may be prevented by a non-electrical film, by an electrical film (electrical charge), or by any combination of the two. An electrical suspension is due to the preferential adsorption of some ion. So long as the particles are all charged positively or all negatively they will repel each other and will not coalesce. Neutralization of the charge causes precipitation through agglomeration.

If we have a suspension which is stabilized by the preferential adsorption of hydrogen ion from hydrochloric acid solution, we have in the solution free hydrogen ions, free chlorine ions, and the adsorbed hydrogen ions which make the suspension behave like a cation though with a different migration velocity from that of hydrogen. If the suspension adsorbs an anion in an amount equivalent to the hydrogen ion adsorbed, the suspended particles will be electrically neutral. We get this by adding an electrolyte, preferably with a readily adsorbed anion. Since we are dealing with selective adsorption, the concentration in the solution of the added anion necessary to cause an adsorption equivalent to the hydrogen adsorption will vary with each anion. Since we are dealing with preferential adsorption, the nature of the cation must have an effect. To put the matter more generally, the amount of an electrolyte necessary to precipitate any given suspension will vary with the nature of the cation, the anion, and

[1] Bancroft: Jour. Phys. Chem., 18, 552 (1914).

the disperse phase. This is not the usual way of stating the case. It is usually considered that only cations count in the case of negatively charged sols, that only anions count in the case of positively charged sols, that the univalent ions all cause coagulation at approximately the same concentration, the bivalent ions at a lower concentration which is practically the same for all bivalent ions, and the trivalent ions at a still lower concentration.[2] The matter has been stated pretty clearly by Höber.[3] "Some general rules apply, among them the law first formulated by Hardy[4] that the precipitation of positive colloids depends chiefly on the anion and the precipitation of negative colloids chiefly on the cation; and also the law formulated a long time ago by Schulze[5] that the precipitating power of the active ion is a function of its valence or of the number of electrical charges which it carries. Of course there are other factors besides these two rules and these factors will now be discussed more carefully; the especial effect of organic ions has already been mentioned."

Everybody recognizes that hydrogen and hydroxyl ions are not to be classed with the other univalent ions because they are usually adsorbed much more strongly,[6] and everybody recognizes that there are other exceptions; but I have found no clear recognition of the fact that Schulze's law is merely a first approximation. In case of doubt it is generally safe to assume that an ion of higher valence will be adsorbed more than one of lower valence; but it is a mistake to consider this so-called law as anything more than a guide. Since we are dealing with selective adsorption we shall expect to find that some univalent ions will be adsorbed by some substances more than some bivalent or trivalent ions. This is shown clearly in data by Odén on colloidal sulphur, given in Table I. In the second column are given the liminal concentrations in gram atoms of the cations per liter necessary to coagulate the sulphur; in the third column are given the reciprocals of these values, the atomic precipitating power so-called.

[2] *Cf.* Freundlich: Kapillarchemie, 350, 354 (1909); Zsigmondy: Kolloidchemie, 54 (1912); Hatschek: An Introduction to the Physics and Chemistry of Colloids, 33 (1913).

[3] Physikalische Chemie der Zelle und Gewebe, 283 (1914).

[4] Zeit. phys. Chem., **33**, 385 (1900).

[5] Jour. prakt. Chem. (2) **25**, 431 (1882); **27**, 320 (1884).

[6] Freundlich: Kapillarchemie, 354 (1909).

TABLE I.

Coagulation of Sulphur at 18°-20°.

Salt	Liminal Value Gram Atoms Cations per Liter	Atomic Precipitating Power of Cation
HCl	6	0.16
$LiCl$	0.913	1.1
NH_4Cl	0.435	2.3
$(NH_4)_2SO_4$	0.600	1.7
NH_4NO_3	0.506	2.0
$NaCl$	0.153	6.1
Na_2SO_4	0.176	5.7
$NaNO_3$	0.163	6.1
KCl	0.021	47.5
K_2SO_4	0.025	39.7
KNO_3	0.022	45.5
$RbCl$	0.016	63
$CsCl$	0.009	108
$MgSO_4$	0.0093	107.5
$Mg(NO_3)_2$	0.0080	125
$CaCl_2$	0.0041	245
$Ca(NO_3)_2$	0.0040	247
$Sr(NO_3)_2$	0.0025	385
$BaCl_2$	0.0021	475
$Ba(NO_3)_2$	0.0022	461
$ZnSO_4$	0.0756	13.2
$Cd(NO_3)_2$	0.0493	20.3
$AlCl_3$	0.0044	227
$CuSO_4$	0.0098	102
$Mn(NO_3)_2$	0.0096	105
$Ni(NO_3)_2$	0.0446	22.4
$VO_2(NO_3)_2$	0.0137	73

Under the conditions of Odén's experiments, sulphur is a negative colloid and the precipitation is therefore due to an adsorption of cations. The first thing to be noticed is that the hydrogen ion is not adsorbed strongly by sulphur, the precipitating power of hydrochloric acid being much less than that of lithium, ammonium, sodium, potassium, rubidium, or caesium chloride. Instead of these univalent cations precipitating at the same concentration, the required concentration of lithium chloride is in round numbers one hundred times that of caesium chloride. The liminal values for barium and strontium are nearly equal, but calcium chloride requires a distinctly higher concentration. If we take the different bivalent ions the values range from 0.0756 for zinc to 0.0022 for barium, a ratio of over thirty to one. The

univalent ion caesium has a greater precipitating power than the bivalent zinc, cadmium, nickel, and uranyl; and about the same precipitating power as the bivalent copper, manganese, and magnesium. The trivalent ion aluminum has about the same precipitating power as the bivalent calcium and distinctly less precipitating power than bivalent strontium and barium. The specific nature of the adsorption comes out extraordinarily clearly with sulphur, practically the only orthodox thing being that nitrate, chloride and sulphate behave practically alike, though even here Odén considers that sulphate has a slight protecting action. This specific nature appears more clearly perhaps if we arrange the cations in order, the one with the greatest precipitating power coming first: Ba, Sr > Ca, Al > Mg, Cs, Mn, Cu > UO_2 > Rb > K > Ni, Cd, Zn > Na > NH_4 > Li > H.

Sulphur is admittedly an extreme case; but Freundlich[7] gives data for colloidal platinum from which I deduce the order: Al, Pb > Ba, UO_2 > Ag > K, Na. Bivalent lead has practically the same precipitating power as trivalent aluminum. Univalent silver is nearer to bivalent uranyl and barium than to univalent potassium and sodium. If more cations had been studied we should very likely have had more distinct evidence of specific action. As it is, it takes 130 millimols NaOH per liter to coagulate the platinum and only 2.5 millimols NaCl. The change from chloride to hydoxide has a more marked effect than the change from sodium to barium. It seems very probable that barium hydoxide would have no greater precipitating power than sodium chloride.

From Pappadà's experiments with colloidal silver[8] I deduce the following order of adsorption: Al > Ba, Sr, Ca > H > Cs > Rb > K > Na > Li. From these data Pappadà concludes that the migration velocity is the determining factor with the univalent cations; but this cannot be true. The difference between aluminum and hydrogen is not very great, one drop of $M/10$ HCl producing a coagulation and one drop $M/20$ $AlCl_3$. In tenth-normal solutions potassium iodide, nitrate, and sulphate produce no coagulation. The reason given by the author is that these anions react with the colloidal silver. In normal solutions the

[7] Kapillarchemie, 352 (1909).
[8] Pappadà: Gazz. chim. ital., **42** I, 263 (1912).

iodides, nitrates, and sulphates are said to precipitate at the same concentrations as the corresponding chlorides and bromides. The effect of concentration is a little obscure in other respects, since 5 or 6 drops of normal KCl precipitate 2 cc. 0.06 percent Ag, whereas it takes only 30 drops $N/10$ KCl to produce precipitation. The essential thing from my point of view is that the different univalent cations have different liminal values; the difference between hydrogen and lithium is greater than that between hydrogen and aluminum.

From experiments on mastic[9] we get the data given in Table II.

TABLE II.

Coagulation of Mastic.

Salt	Liminal Value Gram Atoms	Atomic Precipitating Power of Cation
NaCl	1.0	1.0
$AgNO_3$	0.125	8.0
$HgNO_3$	0.00125	800
HCl	0.010	100
$CaCl_2$	0.025	40
$BaCl_2$	0.025	40
$ZnSO_4$	0.050	20
$Al_2(SO_4)_3$	0.0004	2500
$Al_2(NO_3)_2$	0.0004	2500
$FeCl_3$	0.0003	3300

If we consider the mercury in mercurous nitrate as a univalent ion, it is very much out of place, precipitating at much lower concentrations than the barium, calcium and zinc salts. Of course the formula should be written $Hg_2(NO_3)_2$ with Hg_2 as a bivalent ion.[10] In this case the precipitating power becomes 1600 instead of 800, which puts it up much nearer the trivalent cations than the bivalent ones. The order of cations is: Fe, Al > Hg_2 > H > Ba, Ca > Zn > Ag > Na. Only three anions are given in the table, so it is impossible to tell what effect the anions have. A good many experiments have been made on mastic with different acids but the degree of electrolytic dissociation varies so greatly as to make these results inconclusive. With Prussian blue Pappadà[11] found the order of the cations to be: Fe, Al, Cr > Ba, Cd > Sr, Ca > H > Cs > Rb > K > Na > Li. Sulphates,

[9] Freundlich: Kapillarchemie, 367 (1909).
[10] Ogg: Zeit. phys. Chem., **27**, 285 (1898).
[11] Zeit. Kolloidchemie, **6**, 83 (1910).

nitrates, chlorides, bromides, and iodides all behaved alike. Practically the same order of cations was obtained for copper ferrocyanide.[12] In the case studied by Pappadà the specific adsorption appears to play a very small part. The data for arsenic sulphide[13] however give us variety enough. The order of cations is Ce, In, benzidine, Al > new fuchsine, crystal violet > quinine > morphine, UO_2, Sr, Ca > Be, Zn, Ba > Mg > p- chloraniline, toluidine > aniline > strychnine > guanidine > H > K > Na > Li. The organic cations come in where they please and play havoc with any rule as to valency. The chlorides and nitrates give practically the same values and the sulphates are not far out of line, though it seems probable that the restraining power of sulphate is rather greater than that of chloride or nitrate. The liminal values in gram atoms of the cation per liter are 0.0056, 0.0066, 0.0086, 0.110 and > 0.240 for potassium nitrate, suphate, formate, acetate, and citrate; from which one can deduce that the order of adsorption of anions is: citrate > acetate > formate > sulphate > nitrate, chloride.

It is a great pity that Freundlich did not try other combinations, such as barium acetate.

From the experiments on hydrous ferric oxide,[14] the order of adsorption of the precipitating anions appears to be Cr_2O_7 > SO_4 > OH > salicylate > benzoate > formate > Cl > NO_3 > Br > I, while the order for the cations is: H > Ba > Mg > Tl, Na, K. The univalent ions do not all behave alike and neither do the bivalent ones; but the upholders of Schulze's law can comfort themselves with the fact that the two sets do not overlap except in the case of hydrogen. There is no such comfort in the case of albumin. I have shown[15] that the probable order of adsorption of anions, so far as known, is: sulphocyanate, iodide > chlorate > nitrate > chloride > acetate > phosphate > sulphate > tartrate, the sulphocyanate ion being adsorbed the most and the tartrate ion the least. Here there is nothing even to suggest Schulze's law, and the firm belief which most people

[12] *Ibid*, **9**, 136 (1911).

[13] Freundlich: Kapillarchemie, 351 (1909); Freundlich and Schucht: Zeit. phys. Chem., **80**, 564 (1912).

[14] Freundlich: Kapillarchemie, 352, 358 (1909); Zsigmondy: Kolloidchemie, 181 (1912); Pappada: Zeit. Kolloidchemie, **9**, 233 (1911).

[15] Bancroft: Jour. Phys. Chem., **19**, 352 (1915).

have in Schulze's law is probably the reason for the marked failure to account satisfactorily for the phenomena with aluminum. With the cations, albumin appears to be fairly orthodox, for the order of adsorption appears to be Th, UO_2 > Cu, Zn > Ca > Mg > Li > K, Na > NH_4, though even here the lithium stands higher in the series than it has been found with other substances.

While there is unquestionably a tendency for ions of a higher valence to be adsorbed more strongly than ions of a lower valence, the experiments which have been cited show that there are many exceptions and that the fundamental rule is that the adsorption is specific both as regards the adsorbing substance and the ion adsorbed.

Since the important thing in the neutralization of an adsorbed ion is the adsorption of an ion of the opposite charge, we may get neutralization when we have a colloid with the opposite charge. In other words, we may neutralize an adsorbed ion with another adsorbed ion instead of by a free ion. The usual statement is that sols having the same charge do not affect each other perceptibly, while sols having opposite charges precipitate each other.[16] Neither of these statements is as accurate as it should be. I shall take up first the case of sols having opposite charges. Positive and negative colloids will precipitate each other when in proper proportions and provided adsorption takes place.[17] I see no theoretical reason why we should not have a positively charged and a negatively charged sol, neither of which adsorbed the other to any appreciable extent. In that case these two sols would not precipitate each other. Since complete neutralization takes place only when one sol has adsorbed the amount of the sol carrying an equivalent amount of the ion having the opposite charge, it follows that the amount of one sol necessary to precipitate a given amount of another sol will vary with the degree of adsorption; it will therefore be a specific property and not an additive one. This can be tested experimentally on data by Biltz, given in Table III.[18]

[16] Freundlich: Kapillarchemie, 444 (1909); Zsigmondy: Kolloidchemie, 56 (1912); Höber: Physikalische Chemie der Zelle und Gewebe, 294 (1914).

[17] Bancroft: Jour. Phys. Chem., **18**, 555 (1914).

[18] Freundlich: Kapillarchemie, 445 (1909).

TABLE III.

1.4 mg gold completely precipitated by

CeO_2	Fe_2O_3	ThO_2	ZrO_2	Cr_2O_3	Al_2O_3
4	3	2.5	1.6	0.3	0.1-0.2 mg

28 mg Sb_2O_3 completely precipitated by

Fe_2O_3	ThO_2	CeO_2	ZrO_2	CrO_3	Al_2O_3
32	20	11	6.5	3.0	2.0 mg

24 mg Ag_2S_3 completely precipitated by

Fe_2O_3	ThO_2	CeO_2	ZrO_2	Al_2O_3	Cr_2O_3
13	6	4	2	2	0.5 mg

Alumina is more effective than chromic oxide in precipitating antimony sulphide and much less effective in precipitating arsenic sulphide. The alumina must therefore be adsorbed more by antimony sulphide than chromic oxide, while the reverse must be true for arsenic sulphide. Cerium oxide is less effective than ferric oxide and thorium oxide in precipitating gold; but is more effective than either of these in precipitating the sulphides of antimony and arsenic. The phenomenon is thus specific, varying with the nature of the two colloids. This seems not to have been realized before. In fact Freundlich[19] says definitely that "one seems to find approximately the same order regardless of what sol is to be precipitated." This statement is true; but it misses the important thing in the experiments which was that the order was not always the same.

We can now take up the case of sols having the same charge. The statement that neither has any perceptible effect on the other is based solely on the fact that no precipitation occurs. We know however that cases of adsorption are not limited to colloids or electrolytes having opposite signs. Charcoal adsorbs both bases and acids. Silver bromide adsorbs silver ions or bromine ions as the case may be. There is therefore no theoretical reason why precipitated hydrous ferric oxide might not adsorb chromic oxide, and *vice versa*. If the precipitated substance will do this there is no reason why the peptonized substance should not. Nagel[20] has recently shown that this does occur and that it accounts for the behavior of mixtures of chromic and ferric salts with excess of alkali. Hydrous chromic oxide is peptonized by caustic potash

[19] Kapillarchemie, 445 (1909).
[20] Jour. Phys. Chem., **19**, 331 (1915).

while hydrous ferric oxide is not. If the chromium salt is present in large amount relatively to the iron salt, the ferric oxide will adsorb the peptonized chromic oxide and be peptonized by it, thereby peptonizing it and going apparently into solution. If the ferric salt is present in excess, it will adsorb the peptonized chromic oxide carrying it out of the liquid phase. It is to be noticed that the chromic oxide, when in excess, acts as a so-called protecting colloid to the iron oxide. Everybody is familiar with the fact that gelatine is adsorbed by colloidal gold, for instance; but that is usually treated under the heading of protective colloids rather than under the heading of mutual action of two colloids. The case of chromic and ferric oxides is merely another illustration of the fact that the distinction between a suspension colloid and an emulsion colloid is now arbitrary and unsatisfactory.[21]

Coming back for a moment to the behavior of two oppositely charged colloids, there is a special hypothetical case which is perhaps worth mentioning. Suppose we have two sets of finely divided particles neither of which adsorbs the other appreciably and let us also suppose that one set of particles adsorbs a given cation very strongly, while the other set of particles adsorbs a given anion very strongly. If we take a mixture of these two sets of particles and add a small amount of the salt of the given base and the given anion, we shall have a colloidal solution which will conduct electricity very well but which will contain no free ions to speak of because, by definition, the cations have been practically completely adsorbed by one set of particles and the anions by the other set of particles. This particular case has not been realized; but an intermediate case seems to have been found by McBain and Martin[22] in sodium palmitate solutions:

"Most authors since Kahlenberg and Schreiner[23] have, as a matter of course, ascribed the conductivity exhibited by soap solutions largely to free alkali hydroxide. In previous papers from this laboratory the same tentative suggestion was made, but it was each time clearly stated that it was only a working hypothesis until these experimental data should be ascertained. Now it is certain that the conductivity of soap solutions is only to a

[21] Bancroft: Jour. Phys. Chem., **18**, 556 (1914).
[22] Jour. Chem. Soc., **105**, 965 (1914).
[23] Zeit. phys. Chem., **27**, 552 (1898).

very minor extent due to hydroxyl ions. Further, on account of the fact that the rise of boiling point in certain soap solutions is practically all required to account for the sodium ions alone,[24] the conductivity cannot be wholly ascribed to simple palmitate ions. The suggestion we made is that we have here a new type of aggregate or micelle the mobility of which, owing to the reasons given in the paper cited, is comparable with that of a true anion. Of course, further investigations are proceeding in this laboratory in order to bring this to the test of direct experiment. Incidentally, the above shows, further, that undissociated soap is present chiefly or entirely in colloidal form."

As I see the matter, the sodium palmitate is hydrolyzed and the hydroxyl ions are adsorbed to a great extent by the undissociated palmitate and possibly by the insoluble palmitate acid also, though this seems less probable. The adsorbing substance thus becomes the anion owing to the adsorbed hydroxyl. From his electrometric measurements McBain[25] considers that there is practically no hydrolysis. Electrometric measurements only show the concentration of hydroxyl ions in solution. I do not believe for a moment that an adsorbed hydrogen ion or hydroxyl ion behaves electrometrically like a free hydrogen or hydroxyl ion. An adsorbed chlorine ion, for instance, would not give a test with silver nitrate. Under these circumstances the electrometric measurements are satisfactory for showing the concentration of hydroxyl ions in the solution; but they are utterly worthless for showing the degree of hydrolysis of sodium palmitate. For the same reason I am very sceptical as to any conclusion in regard to albumin solutions which is based on electrometric measurements.[26]

The adsorption of an ion by a colloid gives us an electrically charged colloid with a migration velocity of its own. This migration velocity, so far as studied is of the general order of magnitude of free ions.[27] Consequently, the presence of a colloid may increase or decrease the conductivity of a solution. Raffo and Rossi[28] found that colloidal sulphur cut down the conductivity of

[24] McBain: Trans. Faraday Soc., **9**, 90; Zeit. Kolloidchemie, **12**, 256 (1913).
[25] McBain and Martin: Jour. Chem. Soc., **105**, 957 (1914).
[26] Bancroft: Jour. Phys. Chem., **19**, 349 (1915).
[27] Zsigmondy: Kolloidchemie, 46 (1912).
[28] Gazz. chim. ital., **42** II, 326 (1912).

sulphuric acid and sodium sulphate solutions very much. Paternò and Cingola[29] also found a marked decrease when tannin was added to a potassium chloride solution. In many cases, however, there was no apparent effect. Of course, if the colloid adsorbs both ions or the undissociated salt,[30] the conductivity will necessarily decrease; we do not know whether the marked change with tannin, potassium chloride and water is due to a change of migration velocity or to a wholesale removal of potassium chloride from the solution. Patten once described what always seemed to me a very interesting experiment. He placed a coarse powder in a dilute solution of an electrolyte, allowed the powder to settle, and measured the conductivity of the supernatant liquid. He then stirred the solution and measured the conductivity again while the powder was suspended between the electrodes, finding an increase in conductivity. The powder adsorbed one ion and of course carried the other down with it when it settled. So far as I know, this experiment has never been published and I cannot give numerical data. My impression is that the paper was presented at the Toronto meeting of the American Chemical Society.

The general results of this paper are:

1. The neutralization of an adsorbed ion is due to specific adsorption. The concentration of a given electrolyte necessary to neutralize the charge on a given colloid will therefore depend on the nature of the cation, the anion, and the colloid.

2. It is inaccurate to say that the cation is negligible in the precipitation of a positive colloid and the anion in the precipitation of a negative colloid, though this statement is often approximately true.

3. Univalent ions are not all adsorbed alike; nor are bivalent ions or trivalent ions. The order of adsorption is specific with each colloid and is not determined exclusively—and perhaps not at all—by the migration velocity or solution pressure of the ion.

4. Since the adsorption is specific, Schulze's law is only an approximation. Certain univalent ions are adsorbed by certain colloids more than certain bivalent or trivalent ions. In many cases there is, however, a marked tendency to increased adsorption with increasing valence.

[29] *Ibid.* **44**, I, 36 (1914).
[30] *Cf.* Wolfgang Ostwald, Gedenkboek aangeboden aan Van Bemmelen, 269 (1910).

5. Mixtures of two sols will not precipitate each other unless adsorption takes place.

6. Since adsorption is specific, the order of precipitation of a negative sol by a number of positive sols will not necessarily be the same for any two negative sols.

7. It is not accurate to say that two sols having the same sign have no effect one upon the other. Adsorption may and often does take place.

8. Hydrous chromic oxide, which is peptonized by caustic potash, may act as a protecting colloid for hydrous ferric oxide, which is not peptonized by caustic potash.

9. Since an adsorbed ion does not necessarily give the reactions of a free ion, electrometric measurements may and do lead to false conclusions when applied to colloidal solutions.

10. It is probable that sodium palmitate solutions are hydrolyzed to a very much greater extent than appears from electrometric measurements.

11. If two colloidal sols did not adsorb each other appreciably and if one adsorbed the cation of a given electrolyte very markedly, while the other adsorbed the anion of the same electrolyte very markedly, the addition of a small amount of the electrolyte to a mixture of the two colloids would produce a solution which would conduct electricity without there being any appreciable amount of substance in true solution.

12. In sodium palmitate solutions, it seems probable that the hydroxyl ions set free by hydrolysis are adsorbed practically completely by the colloidal soap.

13. Addition of a colloid to a solution will increase or decrease the conductivity if the adsorbed ion has a greater or lesser migration velocity than the ion adsorbed. In so far as both ions are adsorbed the conductivity will decrease.

14. When adsorption by a colloid causes hydrolysis, the conductivity will depend also on the nature of the products of hydrolysis.

Cornell University.

DISCUSSION.

W. R. WHITNEY: Some one asked what is adsorption. I can not accurately differentiate between absorption and adsorption. We usually have adsorption in the phenomenon going on at a surface when something comes to it and clings there. But a sponge is made of a lot of interior surface, therefore a sponge would adsorb and possibly not absorb. I think you will find the water is held on the surface in the pores. Glass surfaces adsorb from solutions; if you analyze the surface solution you will find the material in the solution has increased in concentration on the surface of the glass.

There is a lot of surface dyeing of fabrics, and in all the dyeing where colloids are the dyeing agents, the dye goes to the surface and sticks there. This is adsorption. Some dyes penetrate the fabric fibres and the process is then one of absorption. So you see it is not easy to differentiate accurately between absorption and adsorption. As the eye gets sharper, we see it more as adsorption.

E. WEINTRAUB: What reason is there for differentiation?

W. R. WHITNEY: I do not know that there is real reason in differentiating. I want to interest young fellows in colleges, if I can, to investigate the colloids. It is one of the most important things in physical chemistry today, one of the most complex, one on which many people are working, and one filled with promise.

I am interested in the bearing of these experiments—upon our knowledge of the phenomena in blood, particularly in the study of immunity from disease. All of these precipitations, the colloidal precipitations, and the immunity phenomena, are probably amenable to the laws of inorganic colloids.

It has been found that an isotonic salt solution continues the pulsations of the excised heart of an animal such as the frog, for considerable periods of time. The action depends not alone on the presence of sodium chloride, but is more satisfactory and endures for much greater length of time as the normal composition of the blood serum is closely imitated. Such a heart would beat a day or more in a solution containing 0.85 percent

sodium chloride, 0.4 percent potassium chloride, 0.4 percent calcium chloride, and about 4 percent dextrose. In this case the dextrose was consumed in the operation. These specific requirements for separate chemical elements recall the specific reactions in the case of the paper under discussion.

S. F. Cox: The importance of colloidal chemistry in biology is very considerable, as has before been suggested. The theories that have been advanced to account for muscular action and rigor, both rigor mortis and calcium rigor, are based upon the coagulation of proteins in the tissue by the action of various electrolytes. A similarity is noted between the values given in Table I, on page 177 of the paper—the atomic precipitating power of the cation and the effects noted when tissues such as muscular tissues are treated with solutions of these salts. Barium and calcium salts cause the muscle to go into rigor almost at once. Sodium and potassium are much slower in effect, but in time produce rigor if the salts be perfectly pure.

A curious thing is noted, in that the effect of one salt, in itself highly toxic, may be balanced by the addition of a small amount of another salt. The action of calcium may be inhibited by the addition of a small amount of sodium or potassium salt.

I should like to ask for an explanation of this balanced action of salts. It is also noted that zinc chloride, a salt normally toxic to tissues, may offset the effects of pure calcium and pure sodium salts. This would seem to indicate that it is not at all connected with the phenomenon of vital force, but is purely a matter of electrolytic and salt action on the protein colloids of the tissues.

W. R. Whitney: I want to enlarge on the point you have raised that you can not confine your conclusions to the fact that calcium produces calcium rigor, and end there. The growth of the body, the composition of bone and muscles and teeth, is all exactly this same thing, and is carried on, not only in protein matter, but in the growth of trees and plants. If you examine any natural organic matter produced by any growth in the world you will find these coagulating and precipitating mineral reagents, calcium, sodium, etc., in the ash of the organic matter; and what the chemist is likely to do for the biologist is to point out that

all his reactions are intimately connected with coagulation by selective absorption of or adsorption by the colloidal matters.

When you look still further you see where you get the electromotive point of view, the production of electromotive force in the heart, for example. In other words, there will be electrical effects in the living body, due to these coagulation reactions. The first early experiments of Galvani on the historic frogs' legs might be explained in this way.

W. S. Franklin: There is a question which has been much in my mind for a number of years in connection with my reading on this subject of colloidal chemistry, namely is it not possible to recover all of the fertilizing values from our city sewage by the use of some kind of coagulant? Considering the phosphorus, nitrogen, and potassium content of our sewage, it might be possible to treat this sewage so as to precipitate all of these substances in a fairly small area near to the outlet, so that they could be recovered. I ask if Dr. Whitney has anything to say as to whether this is possible or not. I asked him as we sat together, what is the composition of the sludge in New York Harbor; whether it does not contain a large amount of potassium and a large part of the phosphorus content of the sewage.

W. R. Whitney: Your question is so complex that I will have to answer that nothing has been done on that complete problem, but work has been done on the specific absorption or adsorption of the coagulating reagent; for example, pure colloidal constituents, like arsenic sulphide, let us say, coagulated by a salt like potassium chloride. We know how much of the potassium chloride it takes to perform the coagulation, and how much of the potassium comes down with the sludge. It is also known that the coagulant which forms the deltas at the river mouths is largely colloidally precipitated matter, due to the concentration of the calcium and sodium in sea water. That is just the reason why the Nile Valley is such a fertile territory. The Nile River overflows and there is a coagulation of this material on the soil of the land.

H. C. Chapin: There was a case of sewage precipitation which occurred in Boston. It was a case of precipitation of colloids,

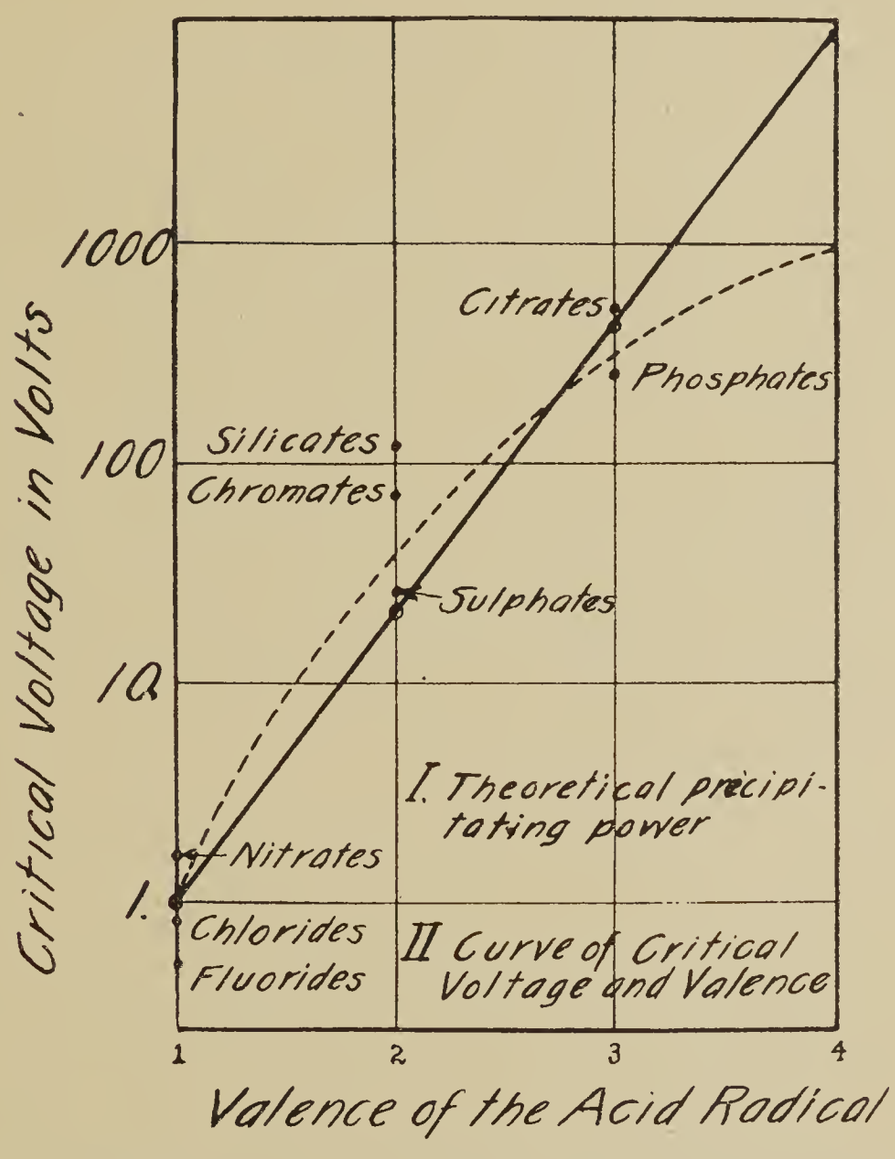
probably, precipitation of the soap contained in the sewage. It occurred in a brook flowing down from the Fenway. Before the dam was constructed across the lower part of the Charles River, the salt water would come up into the Charles, and in this way into the brook. The sewage contained in the brook came in contact with the salt water, probably the soap precipitated, and they had a bad time getting this sludge out of the brook. They were not able to take it out directly at that point, but had to put scows on the Charles River, to clear out several hundred yards from the shore, and pump this sewage from the bottom of the small brook into the scows waiting for it out in the middle of the Charles River, and in that way they took it out to sea.

Wm. R. Mott: The importance of colloidal chemistry has been referred to as regards sewage coagulation.[31] I am very much interested in Dr. Bancroft's paper and wish that Dr. Patten and other of the Government experimenters were here to discuss it. It may be of interest to call attention to one of the places where I have found the theory of effect of valence in colloidal chemistry very useful.[32] This was in the successful prediction of useful electrolytes for aluminum condensers, rectifiers, etc. At an aluminum anode, there is formed on the surface first aluminum hydroxide which is compacted under the coagulating influence of the electrolyte (and current) into a hard insulating film. The power to coagulate aluminum hydroxide and to form insulating films depends chiefly on the acid radical being of high valency. (The metal radical in this case is of minor importance.) The salts of monovalent acids are very inefficient. Chlorates, thiocyanates, nitrates, acetates, formates, chlorides, fluorides, etc., belong to this class of inefficient electrolytes. The salts of bivalent acid radicals are fair insulators, as for example sulphates, chromates, carbonates and tartrates. Trivalent acid radicals, or those of higher valency, are excellent insulators. The phosphates, citrates, borates, arsenates, and molybdenates give very high

[31] See article on Colloids and the Ultramicroscope, by Jerome Alexander in Am. Inst. Chem. Eng. **2** p. 227, 1909, also Pöschl's book on the Chemistry of Colloids page 105 and "The Organic Colloids of Sewage," by J. H. Johnson. J. Roy. San. Inst. **27**, 521-548, 1907. Lime and aluminum sulphate and ferric sulphate are commonly employed in water purification. The action is partly colloidal precipitation and partly entanglement. (Specifications for purchase of $Al_2(SO_4)_3$ as a coagulant at Bangor, Me., filter plant. Eng. Record **64**, 458, 1911. Use of iron sulphate at the Cincinnati Water Purification Plant, Manahan and Ellms, Eng., Rec. **55**, 430, 1907).

[32] See article on Colloidal Precipitation upon Aluminum Anodes, Electrochemical Industry **2**, p. 444, 1904.

critical voltages. The predictions about arsenates and molybdenates have been verified by some English experimenters.[33] Last year Skinner and Chubb illustrated the use of silicate solutions, going to very high values. In such complex cases, it is difficult to arrive at exact relations to valence because of the effect of mixtures. In a mixture of electrolytes, the insulation depends



Precipitating Power of Salts with Acid Radicals of Increasing Valence.

most upon the least effective component. In any case, the valence theory of colloids has here served a useful purpose but leaves considerable to be explained by specific chemical influences. (See diagram.)

Referring to Dr. Bancroft's paper it will be observed in Table I that the specific influence of the alkali and alkaline-earth salts increase in a regular way with atomic weight, indicating that

[33] Bairsto and Mercer, Trans. Faraday Soc. 7, 1-29 (1912).

the periodic law applies here satisfactorily. At the same time, the latent valence of both series is highest with the metals of highest atomic weight. For example, potassium forms KI_3 and the calcium atom can even unite with five halogen atoms. Barium also forms the very stable peroxide. Hence the precipitating power of these elements is perhaps associated with their power to form addition compounds.

In conclusion, I ask if Dr. Bancroft has data on the action of uranium nitrate (and salts) on albumen coagulation.

Francis C. Frary: I would ask if anyone knows whether there is any relation between the phenomenon of adsorption by colloids and the peculiar hydration phenomena where we have a number of salts or ions absorbing water in a solution, and also the hydration phenomena that you get with some of these same colloids absorbing water? A very strange example of the latter is found in one of the photo-engraving processes, where they mix glue and gum arabic solutions together, each colloid having a strong and specific affinity for water; you can get an emulsion of the two if you do not have water enough present to satisfy both, and the size of the suspended droplets and the substance composing them depend on the quantities of the colloids and the amount of water you have present.

Is such an adsorption simply the hydration of molecules of colloids and ions, or is it entirely electrical in its nature, or a case of an extra valence as Mr. Mott suggested?

President Lidbury: I should like to emphasize what Dr. Whitney started out by saying, that thorough investigation is more important today in colloidal chemistry than in any other branch. It is a branch of chemistry which bears such direct relation to electrochemistry that we have a particular interest in it. This, on the theoretical side. The number of fields of applied chemistry that it touches is enormous. Now, the biological chemists have taken this subject and made it, in a certain sense, their own. A good deal has been said this morning about the results which have been obtained, but many of us know of unpublished work which is being carried on today in these fields by biological chemists which promises to lead to absolutely revolutional ideas. Electrochemists ought to make the subject their own also, in

the same sense as the biological chemists have done. It is true that it does not bear such a fundamental relation to our elementary problems, but we have many problems of considerable importance for the solution of which we must apply the methods and results of colloid chemistry. To take only one instance, there is the influence of colloids on metal deposition. In regard to this, we have volumes of unrelated facts, and as work continues papers are being continually presented at these meetings which only add to these facts without contributing in the least to their correlation or explanation. What we need is investigation along lines which will go to the bottom of these phenomena instead of continually adding to the list of what we call "addition substances"—a phrase which covers a multitude of ignorances. We ought not to be satisfied without a complete insight into the mechanism of phenomena which touch so many of our important problems so closely.

We listened yesterday to Dr. Northrup's opinion that no more altruistic work could be done than the work which was done in college laboratories on engineering data. Many of us, however, believe that far more altruistic work could be done in college laboratories in the investigation of the laws underlying little understood phenomena, the practical importance of which is so great.

A. M. Williamson: In connection with the question asked regarding sewage, I came in touch with a process a little while ago which may be of interest. It was an electrochemical installation for purifying sewage. In the simple way in which it was demonstrated, the current was passed between aluminum plates, oxidizing the organic matter in the solution (demonstrated by decolorizing ink), and the material in suspension was thrown out in a heavy flocculent precipitate, which settled rapidly, leaving a perfectly clear solution. I think there is an installation now running treating a million gallons of sewage per day. The recovery of by-product has not been considered as far as I know, but I thought I would mention the process as the question of sewage treatment was brought up.

W. D. Bancroft (*Communicated*): Work along the lines suggested by Mr. Franklin has been carried out in Germany, but

the efficiency was too low to enable the process to get beyond the patent stage. See Jour. Phys. Chem., **19**, 302 (1915).

The theory of the antagonistic action of calcium and sodium ions has been worked out by Dr. G. H. A. Clowes, and I hope that he will publish his work before long.

A paper presented at the Twenty-seventh General Meeting of the American Electrochemical Society, at Atlantic City, N. J., April 23, 1915, President F. A. Lidbury in the Chair.

THE COAGULATION OF ALBUMIN BY ELECTROLYTES.

By Wilder D. Bancroft.

The recent work on albumin has been to the effect that definite compounds are formed with acids and bases.[1] In so far as albumin is present as a second phase, conclusions based on conductivity measurements are subject to serious error and conclusions based on electrometric measurements may be in error. In so far as albumin is present as a second phase, adsorption phenomena must play some part. It seems desirable therefore to see to what extent the coagulation of albumin by electrolytes can be accounted for without postulating the formation of definite compounds. It will then be possible to see to what extent one must postulate the existence of compounds. In other words, we will give up, for the time being, the dogma that albumin is an amphoteric electrolyte.

We start with the assumption that a slightly acid or slightly alkaline solution of albumin is a two-phase colloidal system which is least stable when electrically neutral. When the albumin adsorbs the anion relatively more than the cation, as in alkaline solutions, it becomes charged negatively and consequently moves to the anode under electrical stress. When it adsorbs the cation more than the anion, as in acid solutions, it becomes charged positively and consequently moves to the cathode under electrical stress. If we take a negatively charged albumin, in neutral or slightly alkaline solution, and add a salt solution, the effect of an adsorption of the anion will simply be to increase the negative charge and consequently to make the colloidal solution more stable. The more strongly adsorbed the anion is, the less readily will the albumin be precipitated by cations. On the other hand the adsorption of a cation decreases the electrical charge and consequently makes the albumin less stable. The more readily

[1] Pauli and Hirschfeld: Biochem. Zeit., 62, 245 (1914).

adsorbed the cation, the lower will be the concentration at which it will cause precipitation. In any given case we shall therefore be able to arrange the cations and the anions in series depending on the way in which they precipitate albumin. It must be remembered that in many experiments with white of egg, the globulin has not been removed,[2] in which case the data refer to the globulin rather than to the albumin. In Table I are some data by Hofmeister[3] for a neutral or slightly alkaline solution. The solutions contained 0.2 g. albumin per 10 cc.; the salt concentrations are given in gram equivalents per liter; the temperature was 30°-40°; the numbers in parentheses give the valences of the anions.

TABLE I.

Concentration in gram equivalents per liter.

		K	Na	NH_4
Tartrate	(2)	1.51	1.56	2.72
Sulphate	(2)	...	1.60	2.03
Phosphate	(2)	1.61	1.65	2.51
Citrate	(3)	1.67	1.68	2.71
Acetate	(1)	1.67	1.69	...
Chromate	(2)	2.67	2.61	...
Chloride	(1)	3.53	3.63	...
Nitrate	(1)	...	5.42	...
Chlorate	(1)	...	5.52	...
Iodide	(1)	No precipitate in		
Sulphocyanate	(1)	saturated solutions		

The ammonium salts precipitate at distinctly higher concentrations than the sodium and potassium salts and therefore, by definition, are adsorbed less than these. There is not much difference between the sodium and potassium salts and it is probably wiser to attribute what little difference there is to experimental error, at least temporarily. This is the more advisable because Pauli[4] considers that potassium salts are less effective than sodium salts whereas Hofmeister's data point to their being somewhat more effective. Since Hofmeister found that lithium sulphate precipitated albumin at an equivalent concentration of 1.54, we conclude that lithium salts are adsorbed slightly more strongly

[2] Pauli: Pflüger's Archiv., **78**, 315 (1899).
[3] Pflüger's Archiv., **24**, 247 (1887)
[4] Hofmeister's Beiträge zur chem. Physiol., **3**, 225 (1903).

than sodium and potassium salts. Magnesium sulphate precipitates at 2.65, which seems to imply that magnesium salts are adsorbed less than ammonium salts. Whether we draw this conclusion or not depends on whether we take the equivalent concentration or the ion concentration as the standard. For equivalent concentrations of sodium sulphate and magnesium sulphate the precipitating concentrations are 1.60 and 2.65. The gram molecular concentrations of sodium and magnesium ions are 1.60 and 1.35 respectively, assuming complete dissociation. On this basis magnesium ions precipitate at a lower concentration than sodium ions. If we do not postulate complete dissociation, the effect is even more striking because magnesium sulphate is dissociated less than sodium sulphate. It seems to me that the ion concentration is the important one because it is the ion which is adsorbed. Consequently, I deduce that the order of precipitation and of adsorption is

$$Mg > Li > Na, K > NH_4$$

when referred to ion concentrations, magnesium ions being adsorbed the most and ammonium ions the least. This point has been overlooked entirely so far as I know, all people putting the precipitating power of magnesium salts below that of ammonium salts. The present way of looking at the matter seems to me more sound theoretically, and it has the advantage of bringing the magnesium salts more nearly in line with the salts of the other bivalent metals.

If we deduce the order of absorption of the anions from the data in Table I we get: sulphocyanate, iodide > chlorate > nitrate > chloride > chromate > acetate > citrate > phosphate > sulphate > tartrate, the sulphocyanate ion being adsorbed the most and the tartrate ion the least. Pauli[5] finds that the tartrate comes in between the acetate and citrate. If so, Hofmeister's determinations with the sodium and potassium tartrates must be in error. Freundlich[6] considers that the concentrations should be given in gram molecular weights per liter instead of gram equivalents in which case one gets Table II.

[5] Hofmeister's Beiträge zur chem. Physiol., 3, 243 (1903).
[6] Kapillarchemie, 425 (1909).

TABLE II.

Concentration in gram molecules per liter.

	K	Na	NH_4
Citrate	0.56	0.56	0.90
Tartrate	0.75	0.78	0.91
Sulphate	...	0.80	1.01
Phosphate	0.80	0.82	1.25
Chromate	1.33	1.30	...
Acetate	1.67	1.69	...
Chloride	3.53	3.63	...
Nitrate	...	5.42	...
Chlorate	...	5.52	...
Iodide	No precipitate in		
Sulphocyanate	saturated solutions		

On the basis of these data the order is sulphocyanate, iodide > chlorate > nitrate > chloride > acetate > chromate > phosphate > sulphate > tartrate > citrate, the sulphocyanate ion being adsorbed the most and the citrate ion the least. Since we are agreed that the ion concentration is what counts, this seems at first the more rational way of arranging the data for a study of the anions. It has the further advantage that ammonium tartrate fits in as it should, whereas it was abnormal in Table I. On the other hand there is the difficulty when comparing chromate with acetate for instance, that the concentration of sodium or potassium as ion is double in the gram molecular solution of chromate what it is in the acetate solution. Since the albumin is negatively charged, it is precipitated by cations and consequently the error introduced in Table II by doubling the concentration of the cation, may be more serious than the error introduced in Table I by an inaccurate formulation of the anion concentration. There was a similar error for the cations when comparing $MgSO_4$ with $Na_2SO_4/2$; but the error due to the change in concentration of the sulphate is relatively small, because this anion is not adsorbed to any great extent. With the anions the case is different and it seems to me that the evidence is not sufficient to enable us to decide conclusively between Tables I and II. It will therefore be safer for the present to consider only those anions which come in the same order in both tables. The order of these anions is: sulphocyanate, iodide > chlorate > nitrate > acetate > phosphate > sul-

phate > tartrate, the sulphocyanate ion being adsorbed the most and the tartrate ion the least.

These deductions as to the order of adsorption of the cations and anions are made specifically to fit the facts and are therefore worthless unless confirmed independently. We can get the needed independent confirmation by considering the behavior of albumin in slightly acid solution. Here the more strongly adsorbed cation will increase the electrical charge and will consequently make the albumin more stable, while the more strongly adsorbed anion will cut down the electrical charge the most and will precipitate the albumin the most readily.

With an acid concentration of 0.01-0.02 *N* HCl Pauli[7] found that the order of anions and of cations reversed, the order for the anions becoming: sulphocyanate > iodide > bromide > nitrate > chloride > acetate. This is as it should be, and the same relation holds with a stronger acid, 0.03 *N* HCl. The behavior of the cations becomes abnormal, however, in the 0.03 *N* HCl solution, the ammonium salts precipitating at a higher concentration than the corresponding sodium salts just as they did in the slightly alkaline solutions. I do not pretend to account for this unexpected shift. The most that can be done at present is to formulate the general principles. A careful experimental study of each case will be necessary before one can be certain what is the cause of special alleged discrepancies.

Copper and zinc salts precipitate negatively charged albumin even at concentrations of $M/1000$ or less, from which we conclude that these anions are adsorbed very markedly. From what we have seen in regard to sodium and potassium salts, we should expect that a higher concentration of zinc iodide would be necessary to coagulate albumin than if one added zinc sulphate. The experiment has not been tried in just this form so far as I know; but Pauli[8] found that addition of sodium iodide or sulphocyanate cut down the precipitation when a very dilute zinc sulphate (0.005 *N*) was used. The order of anions was chloride > nitrate > bromide > iodide > sulphocyanate, the most precipitate occurring with the chloride and the least with the sulphocyanate. Curiously enough it was found that iodide kept the solu-

[7] Hofmeister's Beiträge zur chem. Physiol., **5**, 27 (1904).
[8] Hofmeister's Beiträge zur chem. Physiol., **6**, 233 (1905).

tion clear when 0.02 N $ZnSO_4$ was used, while sulphocyanate caused a heavy precipitate. With 0.1 N $ZnSO_4$ the addition of sodium salts caused a precipitate decreasing in the order: sulphocyanate > iodide > nitrate > chloride > sulphate. This is what one would expect if one had a positively charged albumin instead of a negatively charged one. Unfortunately this point was not thought of by Pauli. I am inclined to believe that this reversal of the anions is connected with the fact that zinc sulphate does not precipitate albumin at all when present in normal to double-normal concentrations.

If we start with a negatively charged albumin and add acid, we neutralize the negative charge and precipitate the albumin. On adding more acid we get the albumin charged positively and peptonized. There is no reason to suppose that this action is confined to the hydrogen cation, and I believe that albumin which is not precipitated by a gram molecular solution of zinc sulphate will be found to be charged positively. In that case the order of the anions would be reversed, as Pauli found. With lower concentrations of zinc sulphate we should expect the reversal to occur first with the sulphocyanate, which is exactly what happened. Szilard[9] finds that thorium and uranyl nitrates peptonize albumin, which is what they should do in case these cations are adsorbed very strongly.

If we start with an acidified solution the addition of zinc sulphate or copper sulphate should have very little effect. Werigo[10] reports that copper sulphate does not precipitate albumin in presence of hydrochloric acid. Unpublished experiments by Mr. H. I. Cole showed that 0.2 cc. $M/10$ $ZnSO_4$ produced a distinct cloudiness when added at 30°-40° to 10 cc. of a slightly alkaline albumin solution (containing globulin). When the solution was acidified slightly it was necessary to add more than 10 cc. $M/10$ $ZnSO_4$ to produce the same cloudiness. Mr. Cole also confirmed Pauli's results that addition of potassium iodide to a slightly alkaline solution of albumin cut down the precipitation by zinc sulphate. He also found that in acidified solutions potassium iodide precipitated at much lower concentrations than sodium chloride.

[9] Jour. Chim. Phys., **5**, 495 (1907).
[10] Pflüger's Archiv., **48**, 132 (1891); *cf.* Hardy: Proc. Roy. Soc., **66**, 110 (1900).

Pauli's results with calcium, strontium and barium salts[11] confirm the hypothesis put forward to account for the effect produced by zinc sulphate. He found that with these salts the order of the anions reverses, and becomes: sulphocyanate > iodide > bromide > nitrate > chloride > acetate, the sulphocyanate causing the most precipitation and the acetate the least. If we assume that the calcium ion is adsorbed sufficiently to make the albumin positively charged, the behavior of the anions becomes normal. As a matter of fact Pauli observed that the solutions became slightly acid, indicating the adsorption of lime.

We have still to consider the reversibility of the precipitation. In neutral or slightly alkaline solution the precipitation by the salts of the alkalies is reversible; the precipitation by the salts of the alkaline earths is reversible if the precipitate is washed at once with water but is irreversible if the precipitate is allowed to stand for a short time in contact with the solution; the precipitation by dilute solutions of salts of the heavy metals is irreversible. In acidified solutions the precipitation by sulphocyanates and iodides is irreversible, while the precipitation by acetates and sulphates is reversible if the acid concentration is very low; for concentrations of 0.03 N HCl the precipitation is irreversible.[12]

The precipitation of a colloid is always reversible in case no coalescence or agglomeration takes place, because one of the standard methods of preparing a colloidal solution is to wash out the excess of the precipitating agent. Now the more strongly the precipitating agent is adsorbed, the harder it is to wash it out and consequently the more nearly irreversible the precipitation is. We could use this qualitatively to account for the difference between precipitation by potassium sulphate and zinc sulphate; but we know that there must be agglomeration or coalescence when albumin is precipitated by lime salts because the precipitate can be peptonized when first formed and cannot be later. Even if we got round this, as we undoubtedly could, it is difficult to see how to apply this explanation satisfactorily to the case of precipitation in acidified solution. It seems more probable that the physical properties of the precipitates vary

[11] Hofmeister's Beiträge zur chem. Physiol., **5**, 27 (1901).

[12] Pauli: Pflüger's Archiv., **5**, 27 (1904); Freundlich: Kapillarchemie, 425 (1909).

under different conditions of precipitation and that the irreversible precipitates are more gelatinous than the others. We know that the so-called Péan de St. Gilles ferric oxide is precipitated by hydrochloric acid or nitric acid in a sandy form which is readily peptonized by water and is precipitated by sulphuric acid in a more gelatinous form which is not readily peptonized in water.[13] There are no data bearing directly on this point; but Pauli[14] has suggested in several papers that salts may change the hydration of suspended albumin.

The only other point to be considered is the behavior of so-called electrolyte-free serum albumin.[15] This shows no perceptible diffusion under electrical stress and is therefore apparently electrically neutral without being instable. Addition of sodium, barium, or calcium chloride does not make the albumin electrically positive or electrically negative. It is not precipitated by salts of zinc, copper, mercury, iron or lead. A mixture of $CaCl_2 + NaSCN$ causes no precipitation, though precipitation takes place if the albumin solution is acidified before the mixture is added. The only way I can account for the stability of the electrolyte-free albumin is to postulate that in the absence of salts the peptonizing action of water is enough to keep the albumin in colloidal solution.[16] To this extent the electrolyte-free albumin behaves like gelatine. This is not impossible, because Denaeyer[17] claims that when albumin is heated in water under a pressure of one atmosphere it becomes soluble again and reacts as uncoagulated albumin. Granted that the electrolyte-free albumin is stable and electrically neutral, as Pauli claims, there is no reason why it should be precipitated by salts of zinc, copper, lead, mercury, iron, or lead, because these salts would give it a positive charge and make it even more stable. I do not know why the chlorides of sodium, barium or calcium do not give it an electrical charge of one sign or the other, nor why the mixture of calcium chloride and sodium sulphocyanate does not precipitate it. The obvious assumption to make is that in the

[13] Bancroft: Jour. Phys. Chem., **19**, 230 (1915).

[14] Pauli and Handowsky, Biochem. Zeit., **18**, 340 (1909); Pauli and Falek, *Ibid.*, **47**, 269 (1912).

[15] Pauli: Hofmeister's Beiträge zur chem. Physiol., **7**, 531 (1906).

[16] It is possible, however, that the electrolyte-free albumin is the external phase in the solution. If so, this would account for some of its peculiarities.

[17] Jour. Chem. Soc., **60**, 1269 (1891).

course of purification the albumin had been so changed by hydration, dehydration or otherwise, that it did not adsorb sodium, calcium, barium, chloride, or sulphocyanate ions to an appreciable extent; but does so after contact with an acid. Colloidal silver bromide has apparently practically no adsorbing power for potassium ions or nitrate ions whereas it does adsorb silver ions or bromide ions. All this is purely speculative and not worth much until there is some experimental evidence forthcoming. It does seem to me however that it will be an easier task to account for the properties of electrolyte-free albumin on the basis of varying adsorption than on the basis of an amphoteric electrolyte.

It is usually considered that albumin constitutes a special case[18] and that it differs fundamentally from colloidal gold, let us say, or colloidal ferric oxide. We are told that positively charged colloids are precipitated by anions and that the nature of the cations is immaterial; we are also told that the cation is the all-important factor in the case of a negatively charged colloid, the nature of the anion being immaterial. This seems to me hopelessly wrong. My whole argument will apply to any colloidal solution where the suspended phase becomes instable when electrically neutral and consequently the nature both of cation and of anion is important. The error has come about very naturally because it was very difficult to prepare a positive gold sol for instance or a negative ferric oxide sol. With a positively charged sol the cations which are less readily adsorbed than the ion causing the charge—usually hydrogen—naturally have very little effect.[19] With a negatively charged sol the anions, which are less readily adsorbed than the ion causing the charge—usually hydroxyl except perhaps in the case of the metals—naturally have very little effect. Once the erroneous belief had taken root, it grew because people either did not test large numbers of cations and anions or ignored the evidence in case they did. I shall discuss this matter more in detail in another paper.

The general conclusions of this paper are as follows:

1. So far as the data go, the coagulation of albumin by salts can be accounted for more satisfactorily on the assumption

[18] Freundlich: Kapillarchemie, 434 (1909).

[19] In extreme cases the adsorption may be so slight as to be negligible.

that we are dealing primarily with adsorption rather than on the assumption that we are dealing primarily with an amphoteric electrolyte.

2. Slightly acid or slightly alkaline solutions of albumin are least stable when the dispersed phase is electrically neutral.

3. Since the sign of the electrical charge depends on the preferential adsorption of cation or anion, the nature of both anions and cations is important.

4. When albumin is charged positively, the most strongly adsorbed anion will be most effective in causing precipitation and the most strongly adsorbed cation in preventing precipitation.

5. When albumin is charged negatively, the most strongly adsorbed cation will be most effective in causing precipitation and the most strongly adsorbed anion in preventing precipitation.

6. If one adds to negatively charged albumin a salt consisting of a readily adsorbed cation and a slightly adsorbed anion, we shall get precipitation at low concentrations and no precipitation at higher concentration; but in this latter case the albumin will be charged positively.

7. While the reversibility of precipitation depends in part on the ease with which the precipitating agent can be washed out, it seems probable in the case of albumin that the physical properties of the precipitate are important as determining coalescence and agglomeration. There are no data on this point.

8. In the case of electrolyte-free albumin one must apparently assume that the stability of the solution is due to the peptonizing action of water in the absence of electrolytes.

9. The coagulation of albumin by electrolytes is a typical and general case whereas the coagulations of gold sols and ferric oxide sols are special cases.

Cornell University.

DISCUSSION.

H. S. TAYLOR: There seems to be one outstanding point in connection with Prof. Bancroft's two papers which I think calls for special mention. The two papers are so closely related that it is hardly possible to separate one from the other. For instance, the general conclusion given on page eleven of the first paper discussed this morning[20] is that the neutralization of the adsorbed ions is due to specific adsorption. The concentration of electrolyte necessary to neutralize the charge on a colloid will therefore depend on the nature of the cation, the anion and the colloid.

Now, looking at Table I on page 196 of the present paper, we find the statement that the concentration in gram equivalents per liter required to precipitate a given colloid is 3.63 gram equivalents in the case of chloride, and 5.42 in the case of nitrate.

Now, it is obvious, with the variation in concentration, that there is nothing like correspondence in the amount of cation present and the amount of anion present in the two cases, and it strikes me there is some specific influence, apart from the nitrate and the chloride, something apart from the ions of the two salts at work. I think perhaps the key to the situation may be found in the remark on page eleven of the first paper[20], as follows: "Of course, if the colloid adsorbs both ions or the undissociated salt, the conductivity will necessarily decrease." I think that is a point which does not appear to have been taken into consideration very seriously. I remember looking up references concerning the undissociated molecule, and the point has not really been studied at all. It is a point which seems to me, in view of the situation, such as is found in the acid catalysis of esters, to be one of considerable importance, because there is obviously some other effect present besides that of the cation and the anion, and the only remaining thing which seems to be in solution is the undissociated salt, which is different in the two cases. The influence of the undissociated salt must be investigated.

It is only during the last year or two that Arrhenius has admitted the proposition that not only was the hydrogen ion catalytic, but that the undissociated molecule itself had a certain

[20] This volume, page 185.

specific activity, which must be taken into consideration. In view of the evidence put forward in this paper it is possible that also in the case of colloid adsorption the undissociated molecule may have some influence. I think there is here a very fruitful theme for study.

FRANCIS C. FRARY: Since the hydrolysis of sugar by hydrogen ions has been mentioned, I would call attention to the work of Armstrong, who has shown that the rate of this hydrolysis is very largely increased by the addition of potassium chloride, while according to the ionic theory this should decrease hydrogen ion concentration, and therefore decrease the rate of hydrolysis.

This same matter comes up in another connection. Some time ago I worked on the salting out of alcohols in water solution by the addition of neutral salts, and in looking over the literature on the subject I noticed that many of our German friends had attempted to prepare lists of anions and cations showing the order of their salting-out power. In those lists the sodium had stronger salting-out power than potassium, and when I tried it out on the same alcohols with different salts and on similar salts with different alcohols, I found it was not true. The phenomenon is the specific effect of the salt on the substance to be precipitated. Because common salt precipitates an alcohol only slightly, and potassium chloride a little more, and potassium fluoride and potassium carbonate alike are powerful precipitants, there is no reason to suppose the same precipitation values attach to the same salts for the next higher or lower alcohol. That is moreover not the case, and the precipitation by salts is specific, depending on the salt itself and the substance being precipitated. It is not a matter of ions, but of salts or substances and their relative affinity for or solubility in each other and water. I was wondering if there was not probably some similar specific effect entering into this colloidal precipitation, rather than the ionic effect alone.

W. R. WHITNEY: I have been asked to explain peptonizing. I will say roughly that it is the reverse of coagulation or precipitation. I suppose it comes from the phenomenon of the action of peptone in digestion. I do not know much about that, but with regard to some of the other ferments I do know a little.

If you take, for instance, a thick starchy paste, and put a little diastase into it (which is made by dissolving in cold water the soluble portion of rye and barley), a very few drops of the aqueous solution will peptonize that starch, that is it goes into solution, and gives immediately a water-thin solution.

W. D. Bancroft (*Communicated*): Adsorption of undissociated salt will undoubtedly have an effect on a colloidal solution; but it is hard to see how it can have any effect on the neutralization of an adsorbed ion. The effect of the undissociated salt may show itself in two ways—perhaps more. It may act in the same way that adsorbed sugar does and prevent coagulation. It may cut down the adsorption of an ion and thereby promote coagulation. It may also act in other ways, at present unforeseen. One reason that there are no data on this point is that it was necessary to get a working theory of the ways ions act before one could find out how undissociated salts modify the action of the ions.

A paper presented at the Twenty-seventh General Meeting of the American Electrochemical Society, at Atlantic City, N. J., April 23, 1915, President F. A. Lidbury in the Chair.

THE FORMATION OF MAGNESIUM SUB-OXIDE IN THE ELECTROLYTIC PREPARATION OF MAGNESIUM.

By Francis C. Frary and Harry C. Berman.

Since Bunsen[1] and Matthiessen[2] first obtained metallic magnesium, a good many men have worked upon the problem of its preparation,[3] but to anyone who tries to make it in the laboratory it is evident that there are many things involved in its manufacture which are not known or understood by persons outside of the plants in which it is made. The purpose of this paper is to describe work undertaken in the hope of finding the cause and cure of some of the difficulties met with in the electrolysis of molten magnesium potassium chloride. Much has been done in this direction by Tucker and Jouard (*loc. cit.*), but we believed that a further study of the process would be worth while.

Early in our work we noticed that after electrolyzing magnesium potassium chloride for an hour in a large graphite crucible the electrolyte on cooling contained numerous dark spots. Upon chopping these out it was found that they reacted vigorously with water, evolving hydrogen. It was at first believed that they contained a sub-chloride of magnesium, analogous to the sub-chlorides of calcium studied by Moissan,[4] Guntz and Basset,[5] and Borchers and Stockem,[6] or else a metallic fog such as is said to be often formed during the electrolysis of fused salts at high temperatures. Subsequent work has convinced us that it is neither of these, but a sub-oxide that is present.

[1] Ann., **82**, 137 (1852).
[2] J. Chem. Soc., **8**, 107 (1856).
[3] Bertrand, Compt. rend., **83**, 854; J. Chem. Soc., **31**, i, 161 (1877); Graetzel, Arch. Pharm., (3), **23**, 233; J. Chem. Soc., **48**, 940 (1885); Lake, Eng. Pat. 14,760, Nov. 13, 1886; J. Soc. Chem. Ind., **6**, 223; Haag, Elektrochem. Z., **12**, 243; Fischer, Dingler Poly. J., **256**, 26 (1885); Roberts, U. S. Pat. 778,270; Seward and Von Kuegelchen, U. S. Pat. 880,489, 868,226, 900,961, 931,092, 935,796; Tucker and Jouard, Trans. Am. Electrochem. Soc., **17**, 249 (1910).
[4] Compt. rend., **127**, 584 (1898); J. Chem. Soc., **76**, ii, 153 (1899).
[5] Bull. soc chim., (3), **35**, 404 (1906).
[6] Z. Elektrochem., **8**, 757 (1902).

Various workers have produced dark substances which they have described as sub-oxides of magnesium. Beetz[7] electrolyzed a solution of sodium chloride between magnesium electrodes, and found a black deposit at the anode which evolved hydrogen in certain aqueous solutions. It seems doubtful whether this is the same substance as that which we have prepared, as the latter evolves hydrogen so strongly as to render its formation at the anode in aqueous solutions apparently impossible. Christamanos[8] obtained a similar deposit by burning a piece of magnesium ribbon in contact with cold glass. Baborovsky[9] repeated the work of Beetz, and concluded that the black substance was either a mixture of magnesium oxide and magnesium or else a true sub-oxide. Gore[10] used a magnesium rod, in contact with a noble metal and surrounded by vapors of organic substances. He obtained a black deposit which he believed was magnesium sub-oxide. It will be noted that in all these cases the supposed sub-oxide was apparently formed by the partial oxidation of magnesium; in our experiments we have every reason to believe that it is formed only by the cathodic reduction of magnesium oxide. We would point out the possibility, however, that the product obtained by the above workers may have been an impure sub-oxide originally produced in the preparation of the magnesium and occluded in the metal; so that instead of forming the substance the investigators perhaps merely demonstrated its presence as an impurity in the magnesium which they used.

In our work we have studied the conditions under which the sub-oxide is formed in the electrolyte, and find that the presence of magnesium oxide is necessary and that the reaction is facilitated by a rise in temperature above the melting point of the electrolyte. We have shown that the decomposition of water by the material is not due to the presence of metallic magnesium or a carbide, and that the active substance is not rapidly changed in the air. We believe that metallic potassium may be eliminated from the list of possibilities, both on account of its power of reacting with the magnesium chloride which was always present in excess, and of the relative stability of the active material. If

[7] Phil. Mag., **32**, 269 (1866); Pogg. Ann., **127**, 45.
[8] Ber., **36**, 2076 (1903).
[9] Ber., **36**, 2719 (1903).
[10] Chem. News, **50**, 157.

the active material were sub-chloride, the absence of the oxide from the bath should have little or no influence on its production. The substance appears to be heavier than metallic magnesium, or the solid electrolyte, and is apparently nearly if not quite insoluble in the electrolyte at the temperatures used. We have been unable to isolate it sufficiently pure for analysis, but believe that its identity has been established.

Experimental.

A number of methods of preparing the electrolyte were tried, in hopes of shortening the rather laborious process usually recommended. It is known[11] that fused calcium chloride readily dissolves both calcium oxide and calcium carbonate, and that passing dry hydrochloric acid through this molten mass rapidly and completely converts these substances to the chloride. Attempts to prepare the electrolyte by drying the ordinary crystalline magnesium chloride, adding potassium chloride, fusing, and passing in hydrochloric acid were unsuccessful, and it appears that magnesium oxide does not react with hydrogen chloride at the temperatures employed.

Attempts to prepare the electrolyte free from oxide by evaporating a solution of magnesium chloride and potassium chloride in molecular proportions, calcining, and fusing in a current of hydrogen chloride also failed. It was found necessary to add ammonium chloride in approximately molecular proportions and conduct the fusion with great care, using a platinum dish and not allowing it to become red hot at any time, in order to get an electrolyte entirely free from oxide. It was found that particular pains must be taken to have the salt thoroughly dry before fusion, and that the addition of hydrochloric acid to the solution when it reached a pasty condition was of value. During the fusion the salt is added in small pieces, each being fused before the next is added.

A crucible made by drilling a three inch (7.6 cm.) hole in a piece of four inch (10.2 cm.) Acheson graphite rod was used as anode. In our first experiments a water-cooled iron rod was used as cathode, in the hope of being able to draw out a stick of the metal, as is done with calcium; but this was found impos-

[11] Unpublished work of Frary and Badger in this laboratory.

sible, so a small graphite rod was afterwards used. The crucible was generally bedded in crushed coke, through which a large alternating current was passed at first in order to melt the salt, and a smaller current later to maintain the temperature. The active material was found in the electrolyte after cooling, in the form of dark spots at or near the cathode.

The gas evolved by some of this active material was collected over water and analyzed in the ordinary way. It was found to contain no carbon dioxide, oxygen, or substance absorbable in cuprous ammonium chloride (acetylene). A combustion showed that it contained about 95 percent hydrogen, the remainder being apparently nitrogen.

Attempts were made to separate some of the dark material in a more or less pure state. For this purpose some of the darker portions of the electrolyte from one experiment were finely ground and passed through a 100 mesh sieve to remove as much as possible of the metallic magnesium, some of which was very finely divided. The fine material was then treated in a separatory funnel with a mixture of bromoform and carbon-tetrachloride in such proportions that most of the powder would float and only a part sink. The floating portion appeared to consist almost entirely of minute globules of magnesium and particles of white salt, with a very little dark matter. The powder which settled was dark brown; and after removing and drying it, it acted more vigorously on water than the original powder, while the upper layer was only slightly active. The lower layer appeared to contain no metallic magnesium. The specific gravity of the liquid used was about 1.90. An attempted analysis of this dark product was spoiled by the accidental loss of the potassium determinations.

The remainder of the electrolyte from the same crucible was transferred to a smaller graphite crucible and melted down in a resistance furnace. On raising the temperature to a white heat, most of the electrolyte filtered through into the coke, leaving a dark, thickly pasty, mass behind. This was found to act vigorously upon water. It was ground to 100 mesh and sieved. By heating this powder in a test tube and shaking it vigorously with some mercury, most of the metallic magnesium was removed as amalgam, but a few small pellets could still be

seen. The resulting powder reacted vigorously with water, very much more so than if it had been all metallic magnesium powder.

Another lot of electrolyte was prepared and electrolyzed in the graphite crucible, using a half-inch (1.3 cm.) graphite rod as anode and the crucible as cathode. Twenty-one amperes at 8-12 volts was used for electrolysis, and the alternating current in the resistor was regulated so as just to keep the electrolyte molten, at a red heat which was barely visible. Spongy magnesium was formed in the crucible, and after removing reacted feebly with water. The spongy mass was dried and returned to the crucible, and electrolysis continued at a bright red heat for half an hour. After cooling, the electrolyte was dark colored and reacted vigorously with water. The necessity of a high temperature for the formation of the sub-oxide, and the consequent advantage in maintaining the temperature at as low a point as possible during the preparation of magnesium are clearly shown.

Part of the electrolyte from this experiment was ground and separated in the bromoform and carbon tetrachloride mixture. The heavy material was dried and analyzed. Found: K = 14.95 percent, Mg = 20.20 percent, Cl = 33.81 percent. This shows more than enough magnesium and potassium to combine with the chlorine, but indicates also the presence of either magnesium oxide or other impurities not determined.

It was evident that a more complete analysis was required, so a new lot of electrolyte was melted down in the crucible and electrolyzed for some time at a bright red heat. This time the crucible was made anode and the rod cathode, but the cooled electrolyte after the experiment was as active as before. It was ground to 200 mesh, separated as before with bromoform and carbon tetrachloride, and the heavy particles analysed, with the following results:

	1	2
Insoluble in HCl	2.01%	2.00%
Chlorine	40.94	40.89
Magnesium	24.41	24.64
Oxides of Fe and Al	1.25	1.18
Potassium	17.46	17.30
Sodium	2.80	2.57
Oxygen (by difference)	11.13	11.42

Calculating KCl, NaCl, $MgCl_2$ and MgO, we find that the analysis is satisfied within the limits of error, and conclude

therefore that in the process of grinding to 200 mesh and separating the material, it has been oxidized and the sub-oxide destroyed. This is confirmed by the fact that, while the original electrolyte reacted vigorously with water, some of the 200 mesh powder was found to react only very feebly. It is perhaps significant that over two-thirds of the magnesium appears as oxide.

In order to ascertain whether the "activity" of the electrolyte could be due to the small globules of magnesium scattered through it, some commercial magnesium powder was treated with a little dilute nitric acid to remove oxide and grease, and the excess of acid carefully neutralized with ammonia. The powder thus cleaned did decompose water to a certain extent, but not nearly so rapidly as a piece of the electrolyte about one-fifth its bulk.

In order to be absolutely certain that a finer subdivision of the metal ("fog") was not present, and that the liberation of the hydrogen was not due to any form of the metal, some anhydrous nickel chloride was prepared, and some commercial absolute alcohol was redistilled after standing with magnesium amalgam for 48 hours. Every precaution was taken to insure that both chloride and alcohol were as anhydrous as possible. It was found that no hydrogen was liberated from the alcohol by either magnesium powder or the sub-oxide. Some of the anhydrous nickel chloride was dissolved in the alcohol, and the solution divided. Upon adding a little magnesium powder to one part, a brown precipitate of nickel was quickly produced. The powdered sub-oxide, added to the other part, failed to produce a precipitate, even on standing some time. We believe that this may be regarded as conclusive evidence that the "activity" of the electrolyte is not due to particles of magnesium or a metal fog in it.

All of the electrolyte used in the above experiments had been made in the course of our experiments upon the methods of its preparation, and although fluid when molten, contained a considerable proportion of magnesium oxide. A new lot was now prepared, using the special precautions enumerated above, and after fusion in platinum dishes was found to be free from MgO, as it dissolved to form a perfectly clear solution in dis-

tilled water. Some of this was electrolyzed as in the previous experiments, except that a cover of asbestos paper was placed over the crucible to protect the fusion from the air. Electrolysis continued for an hour and a half at a bright red heat. The current was 20 amperes, and the voltage remained about 7 throughout the run. Upon pouring out and cooling, one globule of magnesium weighing 5.5 gm. was found, together with a number of smaller globules. There were only a few dark spots in the solid mass, but these decomposed water vigorously. The spent electrolyte showed the presence of some MgO, evidently formed by the oxidation of the metal or the hydrolysis of the salt by the moisture of the air during the electrolysis.

In order to prevent the formation of both the oxide and the sub-oxide, a fresh lot of the electrolyte was melted down in a current of dry hydrogen chloride, and electrolyzed at as low a temperature as possible for an hour, during which time the passage of the hydrogen chloride was continued. The current was 20 amperes, the voltage about 10, and the temperature about 450° C. Upon breaking the circuit a counter E. M. F. of 2.6 volts was observed, and this may be taken as the probable decomposition voltage of the electrolyte at that temperature. A portion of the electrolyte was now withdrawn, cooled, and placed in water. No gas was evolved and it dissolved to form a clear solution, indicating that no MgO had been formed so far in the electrolysis, and apparently no sub-oxide or other subsalt. The temperature was now raised to a bright red heat by increasing the heating current (A. C.), and the electrolysis continued with 20 amperes for another hour. The voltage dropped to 8, on account of decreased resistance. The current of dry HCl gas was continued. After pouring and cooling, it was found that the spent electrolyte acted only very slowly on water and showed no dark spots. The slow evolution of hydrogen was undoubtedly due to the small globules of magnesium suspended in the melt, and was markedly different from the action of the dark electrolyte previously obtained. A test of the cooled spent electrolyte showed that there was no MgO in it, even after this long electrolysis.

In order to be sure that no other impurity could be the cause of the formation of the "active" material, this same electrolyte

was now melted down in the open crucible, and some magnesia usta (basic carbonate) was added. It was now electrolyzed at a bright red heat for an hour and a half, using 21 amperes at 10 volts. After cooling the electrolyte showed a large "activity," when placed in water. It would seem that an extra large amount of the sub-oxide might have been expected to form here, on account of the quantity of oxide added, but no difference was apparent between this electrolyte and those obtained previously by electrolysis of the salt containing only a moderate amount of the oxide, so it is believed that only a small amount of MgO is necessary in the electrolyte to cause the formation of the sub-oxide, and that the amount of this substance which can exist in the electrolyte under the conditions of the experiment is relatively not large. This is easily explained by assuming that it is either oxidized at the anode or further reduced to metal at the cathode. Both of these reactions are of course possible, and positive evidence in favor of the oxidation of the substance at the anode is seen in the fact that the electrolyte around the latter was always white and free from the sub-oxide.

Attempts to produce the sub-oxide by the action of metallic magnesium on the oxide were not successful. Some of the double salt which was known to contain considerable oxide, and which upon electrolysis yielded sub-oxide, was heated for some time at a bright red heat with considerable magnesium powder. The resulting mass showed no dark areas and was only very slowly acted on by water, indicating that the magnesium particles (which had not agglomerated into a mass) had not reacted with the oxide or with the double salt.

Summary and Conclusions.

Magnesium sub-oxide is formed during the electrolysis of magnesium potassium chloride if magnesium oxide is present. A high temperature facilitates its formation. It is dark colored, heavier than either metallic magnesium or the double salt, decomposes water vigorously, is oxidized (if finely ground) in the air, and is apparently re-oxidized at the anode in the bath.

Magnesium sub-oxide can not be formed by the reaction of magnesium (metal) on the oxide in the presence of the molten

double salt at a bright red heat, and is apparently only formed under such conditions by the electrolytic reduction of MgO.

Magnesium sub-oxide does not react upon a solution of anhydrous nickel chloride in absolute alcohol, while metallic magnesium does.

There is no evidence of the formation of a "metal fog" during the electrolysis, even at a bright red heat, and the dark appearance of the electrolyte under these conditions is due to the presence of the sub-oxide.

Magnesium oxide dissolved or suspended in molten magnesium potassium chloride does not react with dry hydrogen chloride, differing in this respect from lime. As the magnesium oxide can not be removed from the electrolyte, its formation must be prevented during both the preparation of the electrolyte and the actual electrolysis.

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DISCUSSION.

C. W. Bennett (*Communicated, read by J. W. Richards*): It seems to me that if these theories of the formation of magnesium sub-oxide by partial reduction of magnesium at the cathode and the oxidation of the sub-oxide at the anode are correct, its formation could be prevented or cut down by stirring the molten bath. If, on the other hand, the difficulty is caused by particles of metal, they would be disseminated throughout the mass and therefore the range of their existence would be increased.

I have always assumed that this behavior of fragments of such electrolytes is due to particles of metal in a very fine state of subdivision. We have noticed this behavior in a number of cases of electrolysis; for instance, in the electrolysis of sodium-aluminum chloride. Particles of metal in a fine state of division, occasioned by their formation in solution and subsequent freezing, will react in peculiar ways. Metals and substances when

obtained by a peculiar method of preparation in a fine state of division will many times take fire spontaneously, although they are not ordinarily oxidized rapidly by the oxygen of the air. As a matter of fact, the results obtained in this paper could be explained on the assumption that when magnesia is present particles of metal are absorbed by or absorb magnesia and are held in colloidal suspension in the melt, while no such colloidal suspension is occasioned in the absence of magnesia or in the presence of hydrochloric acid. Where the colloidal particles are present, the material is very active; where absent, the material is not so strongly active.

President Lidbury: I would like to ask Dr. Frary if it has been possible to prepare this material from a magnesium chloride bath containing no potassium or sodium?

Francis C. Frary: That kind of a bath is extremely difficult to prepare and to work. We tried to get some anhydrous magnesium chloride, but were unable to get a sufficient quantity of the pure material to work on; so I do not know. Your idea would be that there might possibly be a potassium compound involved?

President Lidbury: Something of that kind.

Francis C. Frary: We thought that was conclusively excluded by the fact that potassium was so much more electronegative than magnesium, having so much greater power of displacing nickel than megnesium.

President Lidbury: Have you demonstrated beyond all possibility that magnesium and potassium alloys will not do it?

Francis C. Frary: No, we have not demonstrated that.

President Lidbury: The acceptance of a new compound, if it is impossible to isolate the compound and prove its existence by analysis, demands the exclusion of every other kind of hypothesis by some kind of definite proof.

Francis C. Frary: The existence of a potassium-magnesium alloy at that temperature, and in a bath which contains half magnesium chloride, is extremely improbable, when you consider the relative affinities of magnesium and potassium for chlorine. It

would seem that the potassium would certainly react with the magnesium chloride. This material is so stable that we took some of the electrolyte and heated it to white heat in a graphite crucible, and almost all the electrolyte seeped away and filtered through the crucible into the coke, leaving this brown material behind in the crucible. Under these circumstances the magnesium-potassium alloy would have reacted, and the potassium would have been absorbed, as far as anybody can reason from our knowledge of such things.

JOS. W. RICHARDS: This is a timely paper, because the industrial manufacture of magnesium will probably begin in this country about the middle of this year. Our supply of magnesium has been cut off by the war, and a plant for manufacturing it is being erected at Niagara Falls by the Aero Metal Company.

H. S. TAYLOR: Has it been definitely proved that you can not get a pure magnesium chloride in bulk by passing dry hydrochloric acid gas over heated magnesium chloride crystals? I remember in 1909 preparing a small quantity of pure anhydrous magnesium chloride under these conditions.

FRANCIS C. FRARY: Undoubtedly you can prepare it in that way, but if you try to prepare it in quantities you have a good deal of work on your hands.

L. D. VORCE: On smelling the water to which Mr. Frary added a little of the sub-oxide to show the evolution of hydrogen, the odor suggests a hydrocarbon gas.

FRANCIS C. FRARY: There is a trace of a hydrocarbon there. We suspected the presence of a carbide, but analysis of 100 c.c. of the gas showed no hydrocarbons which could be determined. It is only a trace, whatever it is.

A paper presented at the Twenty-seventh General Meeting of the American Electrochemical Society, at Atlantic City, N. J., April 22, 1915, President F. A. Lidbury in the Chair.

ON THE TEMPERATURE OF REACTION BETWEEN ACHESON GRAPHITE AND MAGNESIA.

By O. L. Kowalke and D. S. Grenfell.

Among the refractory materials for electric furnace construction, magnesium oxide, with a melting point of 2,800° C.,[1] and carbon, with melting point above 3,500° C., have been found satisfactory and quite indispensable. In the construction, however, they must frequently be in contact with one another, and at high temperatures several investigators have observed a reaction between these two materials.

In August, 1905, while melting some iron alloys in a granular carbon resistor furnace with walls made of magnesia brick, O. P. Watts[2] noticed that the carbon seemed to shrink in volume and that a black, soot-like deposit about one-half inch thick appeared on the interior walls of the furnace. This crust was first thought to be due to impurities in the resistor, but the substitution of other forms of carbon did not decrease the loss. He decided that the reaction was a simple reduction of the magnesia by the carbon and that it was reversible, basing his conclusions upon a chemical examination of the condensed product.

The same phenomenon was observed later by H. M. Goodwin and R. D. Mailey[3] when attempting to fuse magnesia in a carbon tube. They found that a black product condensed on the cooler part of the tube and determined that it was not a carbide, but did not fix its identity.

A study of this phenomenon was made by P. Lebeau[4] in an attempt to determine the nature of the reaction and to confirm

[1] Melting Point of Some Refractory Oxides. Bur. Stand. Bull., **10**, (No. 212), 18.

[2] Action of Carbon on Magnesia at High Temperatures. Trans. Am. Electrochem. Soc., **11**, 279-89 (1907); Chem. Zeits., **31**, 739.

[3] Physical Properties of Fused Magnesia. Trans. Am. Electrochem. Soc., **9**, 90 (1906); Phys. Rev., **23**, 22.

[4] Reduction of Magnesia by Carbon. Compt. Rend., **144**, 799-801; Rev. Electrochem., **1**, 156-7.

the results obtained by the other investigators. His final decision was that a carbide of magnesium was formed.

R. E. Slade,[5] while carrying on an investigation with the same end in view, confirmed the opinion of Watts and of Goodwin and Mailey, and in addition found that the reaction in the case of the materials he used began at 1,700° C.

While determining the temperature of fusion and volatilization of magnesia on a base of carbon, a violent reaction was reported by Ruff, Seiferheld and Suda[6] at 2,000° C. With a graphite base, however, there could be observed no appreciable reaction below the fusion temperature of the magnesia, which they give at 2,500° C.

The present investigation aimed at the determination of the temperature at which carbon, in the form of Acheson graphite, will react violently with magnesia. Some preliminary work was done in 1913, but the present article covers the results of work done during the past year. Two sets of data were in reality obtained—a set made during the spring of 1914, and another, with different apparatus and pyrometer, during the fall of 1914. The data obtained at the two times are an excellent agreement.

Methods.

In the solution of this problem, three distinct methods of attack were pursued. In the first method, weighed samples of the two materials—magnesia and graphite—were heated in contact with each other for about half an hour at various temperatures and the loss in weight determined. It was thought that a decided increase in the loss would result at the temperature of violent reaction. This method failed in its purpose because of the fact that it was almost impossible to maintain the furnace at a constant temperature for more than a few minutes. These runs did indicate, however, that the reaction proceeds according to the equation

$$MgO + C \leftrightharpoons Mg + CO$$

[5] Reduction of Magnesia by Carbon. Proc. Chem. Soc., **24**, 29; Chem. Soc. Jour., **93**, 327-33.

[6] Researches in the Realm of High Temperatures: I. On the Fusion and Volatilization of Our Most Refractory Oxides in the Electric Vacuum Furnace. Zeits. f. anorg. Chem., **82**, 373-400; (Abst.) Silikat. Zeits., **1**, 212.

because the ratio of the losses MgO/C was approximately the theoretical, according to this equation, as shown in the accompaying table:

TABLE I.

Run No.	MgO Loss	C Loss	Ratio of MgO/C (Theoretically 3.33)
3	3.68g	1.05g	3.50
4	2.41	0.66	3.65
5	3.35	0.95	3.53
7	4.38	1.16	3.78
8	0.65	0.23	2.83
9	9.43	2.71	3.48

The second method was based on the fact that the reaction from left to right is endothermic. When the substances attain the reaction temperature there will be heat absorbed from the surroundings which will result in a fall of temperature. This method yielded some excellent results, as shown in Figs. 4 and 5.

After the temperature had been determined, some data on the rapidity of the reaction seemed desirable. The materials were heated in a vacuum furnace of the Arsem type, provided with a mercury manometer for determining the pressure inside the furnace. If the gas, carbon monoxide, were formed, the pressure would increase suddenly at the temperature of reaction and would be an indication of the rapidity of the reaction. The experiments with the vacuum furnace indicated no great rise in pressure, and the usual deposition of carbon and magnesia was observed. This provides additional evidence of the reversibility of the reaction; for had it not reversed, the pressure should have increased, due to the formation of carbon monoxide. As soon as the products of the initial reaction reached the outer, cooled portions, the magnesium reduced the carbon monoxide to amorphous carbon and the two solids were as in the beginning.

Apparatus.

The observations of temperature were made with an optical pyrometer of the Holborn-Kurlbaum type, equipped with a series of revolving sectors for high temperature work, as suggested by Mendenhall.[7] In the calibration of this instrument the standard

[7] Notes on Optical Pyrometry. Phys. Rev., 33, 74.

was a platinum and platinum-rhodium thermocouple certified by the Bureau of Standards. For the calibration of the optical pyrometer a specially constructed "black-body" tube furnace was used. The E.M.F. of the couple was measured on a Leeds and Northrup Type "K" potentiometer, and the current in the pyrometer lamp on a Weston ammeter, calibrated in the State Standards Laboratory.

The calibration was conducted at one known temperature by the method of Prof. C. E. Mendenhall[8] applying Wien's Distribution Law

$$\text{Log } J = K_1 - \frac{K_2}{T} \quad \ldots\ldots\ldots\ldots(a)$$

If a rotating sector be interposed between the source of light and the pyrometer, such that the intensity is reduced by a factor $\frac{1}{S}$, the above equation becomes

$$\text{Log } \frac{J}{S} = K_1 - \frac{K_2}{T_s} \quad \ldots\ldots\ldots\ldots(b)$$

By subtraction (a—b),

$$\text{Log } S = K_2 \left(\frac{1}{T_s} - \frac{1}{T}\right) \quad \ldots\ldots\ldots\ldots(c)$$

By taking a number of discs and obtaining corresponding values of current through the pyrometer lamp filament, a series of values of T_s can be computed which correspond to the temperatures which would be obtained with an open objective.

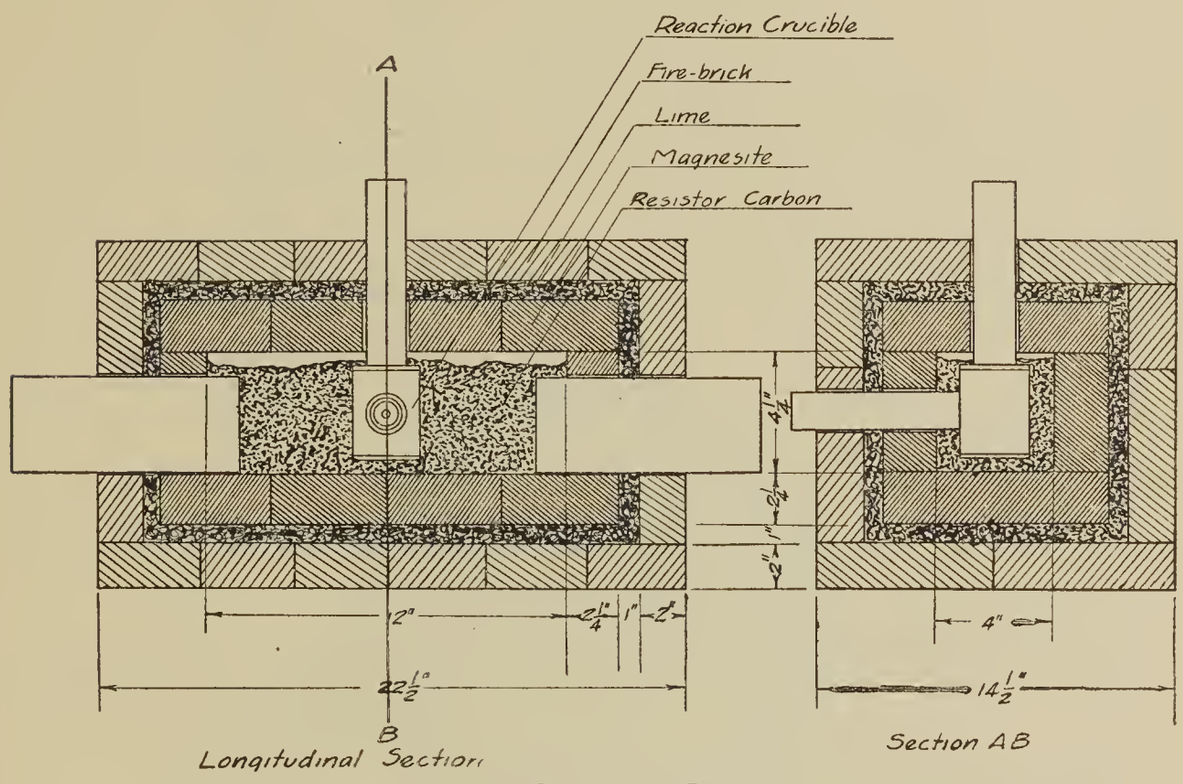
In this way, values of T_s were obtained for the various sectors, and were plotted on co-ordinate paper. This gave a calibration curve for an open objective. Then, to obtain the calibration curve for a given sector, the proper value of S was substituted in the equation (c); the value of T_s was obtained from the above-mentioned curves for a given current value, and the temperature T corresponding to that current was computed.

For example, on the open-objective calibration curve, a current of 700 milliamperes corresponds to a temperature of 1,253° C. or 1,526° absolute.

[8] Notes on Optical Pyrometry. Phys. Rev., 33, 74.

Furnace.

The special furnace employed in this work was a resistor furnace constructed of magnesia brick, insulated with air-slaked lime and fire brick, as shown in Fig. 1.



SPECIAL FURNACE

FIG. 1.

Reaction Crucible.

The reaction crucible shown in Fig. 2 was turned from a rod of Acheson graphite, and was provided with a sight tube for the pyrometer observations and a chimney for the escape of the products of the reaction. Various modifications of this idea were tried in the course of the researches, but in the final form the chimney was made very large in comparison with the size of the crucible. The magnesia rested on a slender support, to prevent any large transfer of heat from the crucible to the magnesia by conduction. (See Fig. 2.) It was found that the heat conducted to the magnesia test specimen through the graphite support frequently spoiled the test, so the stem of the support was made small to compel heating by radiation. The materials of the reaction were the purest attainable. The magnesia was some of the electrically fused magnesia made in this laboratory. The graphite specimen was machined from a solid rod of Acheson graphite.

At first the magnesia sample (about 5 g.) was placed inside the reaction chamber on a small graphite support before the end

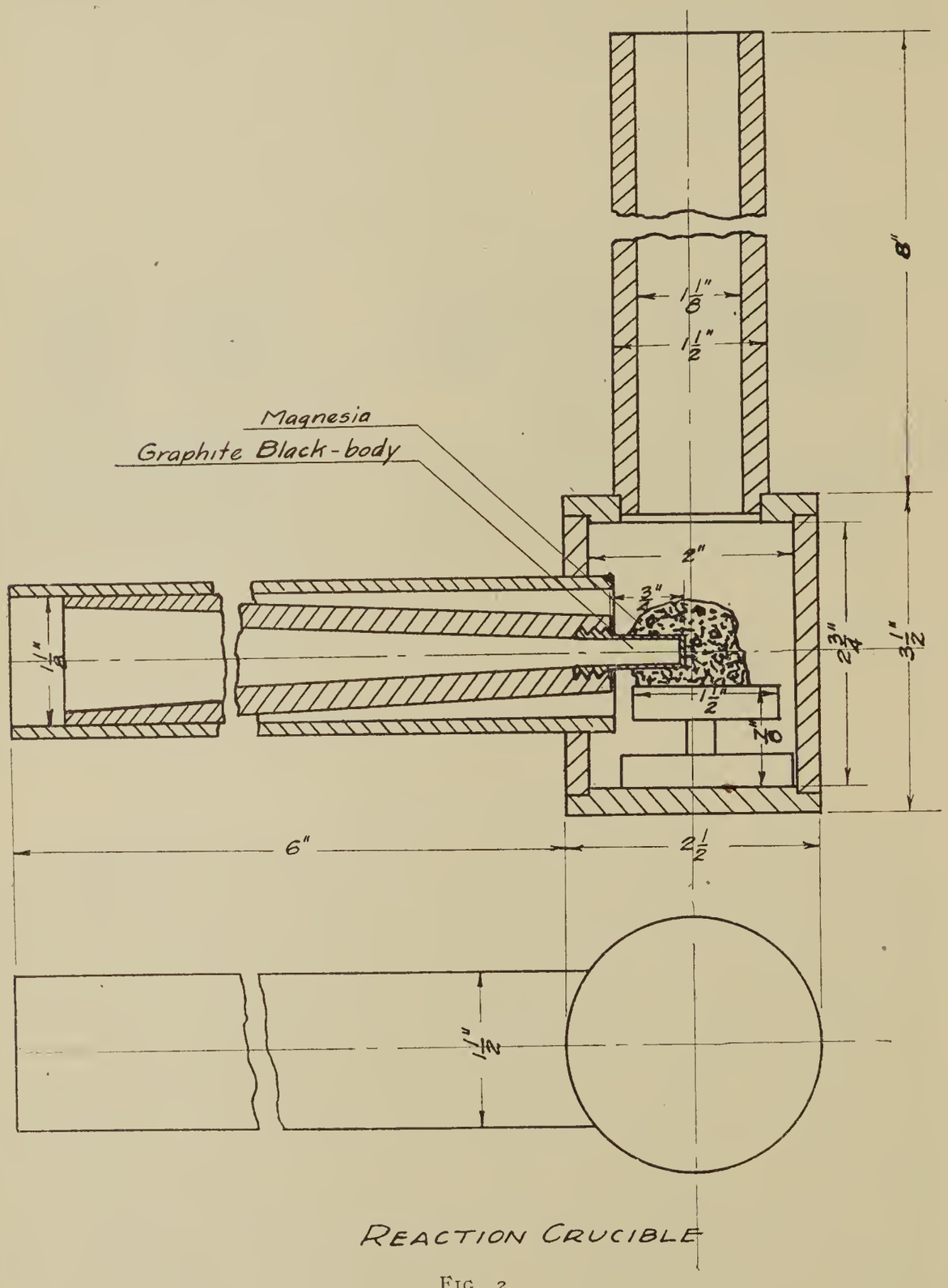


FIG. 2.

of the "black-body" tube. Next, a larger sample (about 15 g.) was used and one side was ground to a plane surface and placed in intimate contact with the end of the black-body tube. Runs

12 and 14 were made in this manner (see Fig. 4). Lastly, the magnesia pulverized to about a 50 mesh and, moistened with water, was molded about the sight tube. The remainder of the runs were all made with this arrangement.

Procedure.

For the first experiments the weighed materials were placed in the reaction crucible and the latter covered with resistor carbon. Bricks were placed on top of this, and lime was added for heat insulation. Power was applied, and temperature, time and current observations were made. No wattmeter was avail-

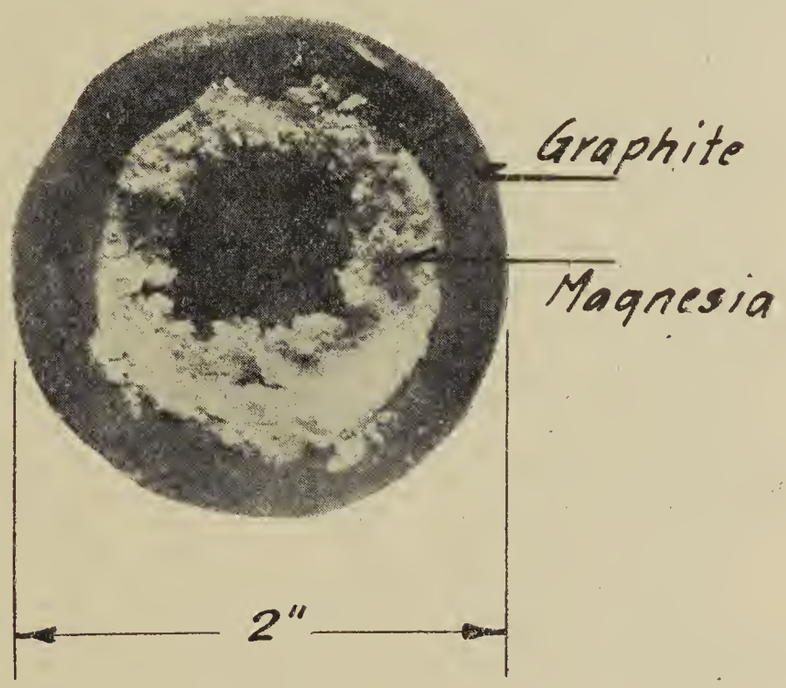
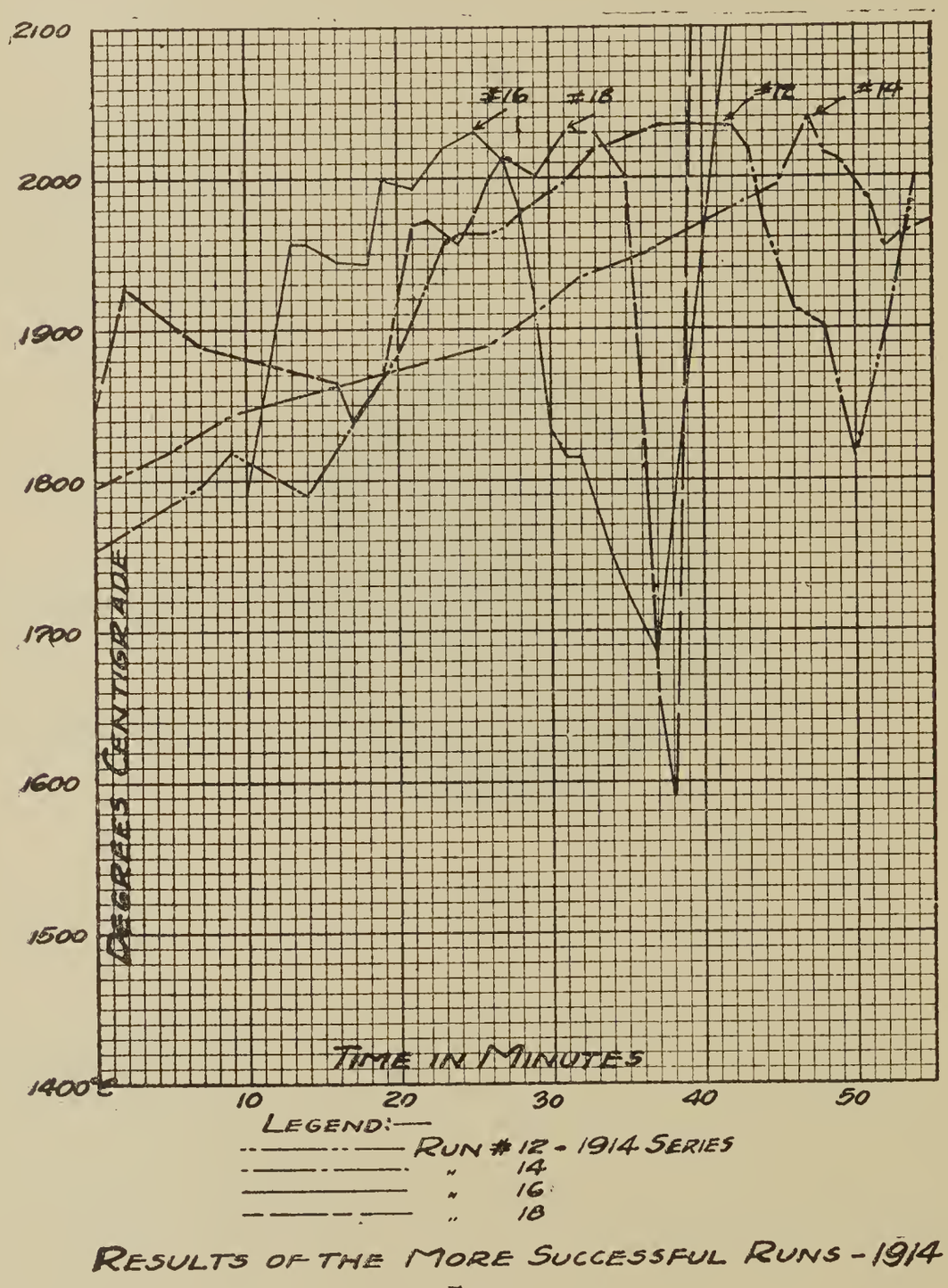


Fig. 3.

able at first, but later one was installed and the power input could then be measured, each run being made with constant input. After the furnace had cooled, it was opened; the materials were removed from the reaction crucible and reweighed. Curves were plotted showing the relation between temperature and the percentage loss in weight. Due to the removal of the resistor carbon after each run, the resistance of the furnace varied greatly from run to run, and a similar power input did not result in the same rate of heating.

The second method of attack required the same apparatus and manipulation, excepting for the omission of the weight data. The recorded data consisted of time, current or power and tem-

perature, as shown graphically in Figs. 4 and 5. Another obstacle was the fume which resulted from the reversed reaction in the cool portions of the furnace. The products of the reaction con-



RESULTS OF THE MORE SUCCESSFUL RUNS - 1914

FIG. 4.

densed in the chimney (see photograph, Fig. 3), and a pressure resulted in the furnace from the stoppage of this exit. As the pressure increased in the crucible, a portion of the magnesium vapor passed through the walls of the pyrometer sight tube, united with oxygen and formed a white fume, reducing the in-

tensity of the light and finally closed the sight tube. It was necessary at frequent intervals to remove the condensed magnesia and amorphous carbon from the chimney by forcing a passage with a carbon rod. At this time an intense bright flame issued from the chimney, showing that the reaction was proceeding with great violence. The fumes from the combustion of the magnesium vapor filled the room with a haze. The chimney was then increased in size to about one-half the diameter of the crucible, but even then it was frequently stopped at the end of the run.

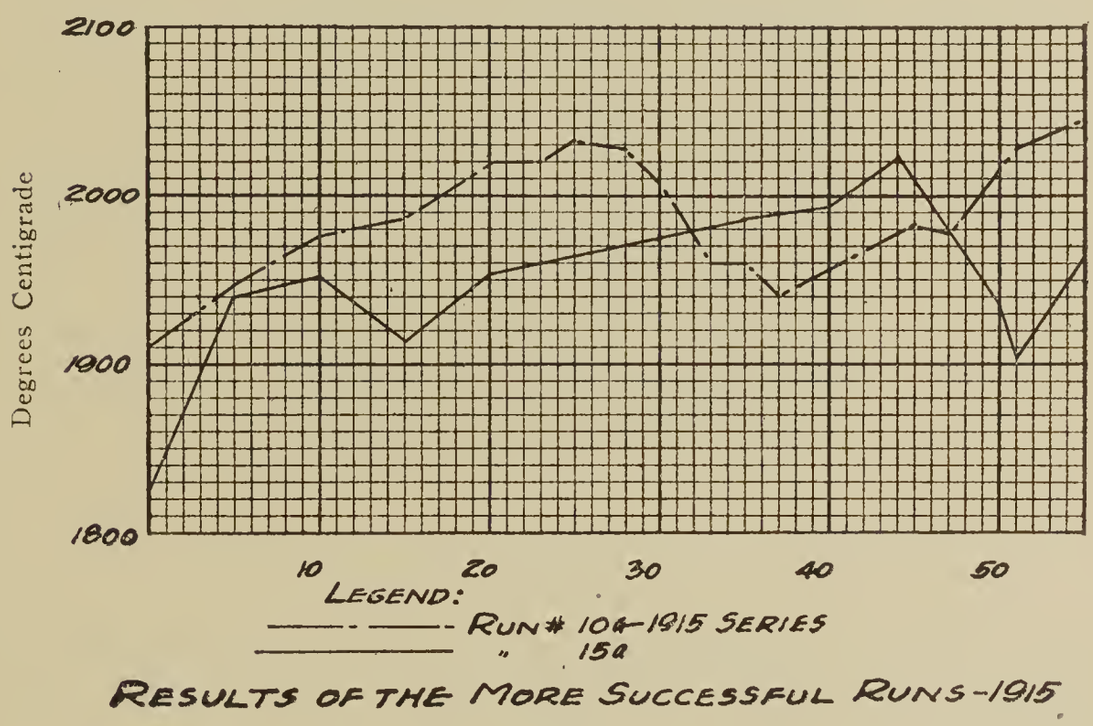
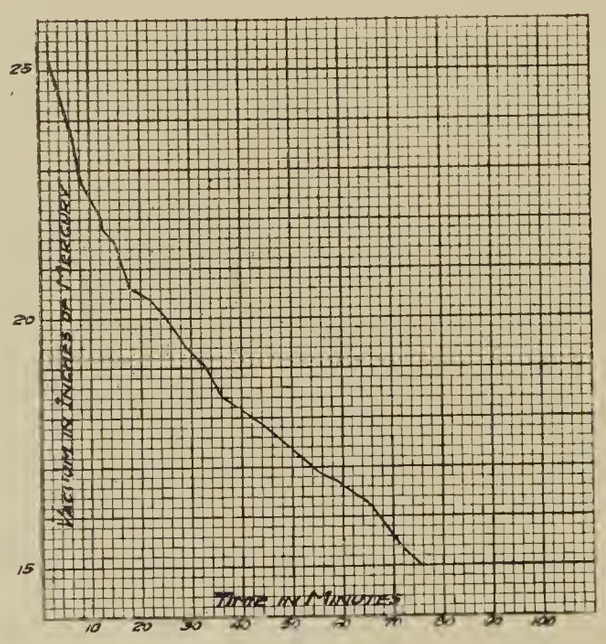


FIG. 5.

For the experiments in the vacuum furnace a small crucible of about one and one-half inches diameter and three inches high was turned from graphite and filled with loose, pulverized magnesia. A cover was provided with a sight tube for the pyrometer. Holes were drilled in the sides of the crucible for the escape of the products of reaction. This was placed within the graphite spiral of the Arsem vacuum furnace and the chamber sealed. The suction was applied and the power circuit closed. Preliminary tests showed that the furnace was fairly gas tight, although there was a slight leakage at the joints of the rubber tubing connections. The evacuation was stopped at a temperature of 1,500°-1,600° C., and observations of time, power, temperature

and pressure were noted. There was a great deal of difficulty in measuring the temperature within the vacuum furnace because of the fume in the furnace and also because of a deposit of condensed magnesia on the inner side of the mica window. For this reason the temperature data secured are not considered reliable.



Run #5v on the Arsem Vacuum Furnace

Fig. 6

Results.

One result of this investigation has been the justification of the original assumption that the equation of the reaction is expressed thus:

$$MgO + C \leq Mg + CO$$

This is proven by the facts:

(1) The ratio of the combining weights is closely that of the equation.

(2) The products of the reaction have all the appearance of being MgO and C (see photograph, Fig. 3).

(3) The pressure of the vacuum furnace does not rise appreciably at the reaction temperature, showing the reversibility.

(4) The extremely bright flame of magnesium burning to magnesium oxide occurred again and again at the reaction temperature, and the collected magnesia formed is characteristic.

The pyrometric results indicate that the reaction commences slowly at about 1,950° C. (this temperature being somewhat dependent on the rate of heating), and becomes very violent at temperatures above 2,030° C. This agrees well with the results of Ruff, Seiferheld and Suda, who found a violent reaction with amorphous carbon at 2,000°.

Since the reaction temperature has been found many times at about 2,030° C., and that with definiteness, it is suggested that this may be a "fixed point" for the calibration of optical pyrometers. This arrangement has the following advantages: (a) can be carried on in presence of carbon, (b) done at atmospheric pressure, (c) no contamination of materials, (d) cheapness of test materials.

Care must be exercised to provide adequate vents to the reaction chamber to avoid a pressure inside which produces fume in the pyrometer black-body tube.

The power in the furnace should be kept constant for satisfactory results.

Chemical Engineering Department,
University of Wisconsin.

DISCUSSION.

C. W. Bennett (*Communicated*): There is no doubt but that magnesia is decomposed by carbon or graphite at high temperatures. It would have been of much more interest to practical electrochemists if Mr. Kowalke had studied the point of break-down of commercial magnesia fire-brick instead of chemically pure magnesia, as we all know that the commercial article is less resistant than chemically pure material.

Granting the decomposition of magnesia by carbon and graphite, the mechanism of this break-down is quite a different proposition.

Let us assume that magnesia is reduced by carbon to magnesium. I do not believe it would be possible to distil magnesium through carbon without forming carbide. As a matter of fact we all know that magnesia and carbon react to form magnesium

dicarbide at approximately 1,700°. Furthermore, a reaction occurs between magnesia and carbon at 1,500°.

From Fig. 6 it would appear that the pressure in the vacuum furnace does rise at 1,600° at least and that an increase of two-fifths of an atmosphere occurred in a little over an hour. There are no data from which it can be determined whether the temperature at this time was higher than 1,600°. As a matter of fact we know that there is an increase of pressure at 1,500°, 1,600° and 1,700°, and carbon monoxide is formed.

In the third conclusion where it is stated that the pressure in the vacuum furnaces does not rise appreciably at the reaction temperature, I think it will depend upon how long the product has been heated below the so-called reaction temperature and above 1,500°. If the charge is completely transformed to carbide by heating for an appreciable time at, say, 1,600°, then run up to 1,950°, there is no reason why there should be an increase of pressure, because the carbide would distil and condense on the cool parts of the furnace without changing the pressure appreciably. We have not yet determined the composition of these carbides, but it is believed that oxidation of the carbides yields free carbon and magnesia. This fact would not be occasioned by carbon monoxide, but would be caused by oxygen of the air upon opening the Arsem furnace. Whether oxidation is possible or not, we have repeatedly demonstrated that it is impossible to open an Arsem furnace and obtain the product as it was formed in the neutral atmosphere. Oxidation always occurs very rapidly. As a matter of fact I have scraped from the cool parts of the furnace a magnesium compound and caught it in the palm of my hand. The heat from the palm of my hand was sufficient to cause the whole mass to take fire spontaneously.

The magnesium flame would be occasioned by the oxidation of such material as well as the oxidation of pure magnesium. It would therefore appear that the conclusions reached in this paper are largely unwarranted and are open to serious criticism.

E. F. Northrup: This paper has had some interest for me, because I found occasion to study the problem of finding a stable material for electrical insulation between slabs of graphite, and to get the information I made some measurements on magnesium oxide, aluminum oxide, and certain other oxides, and I have a

few facts which may be of interest, which I will presently give.

Before doing so, I wish to suggest a possible means of studying the moment at which violent reactions begin. An arrangement which I have already described in Metallurgical and Chemical Engineering, February, 1914, enables one to be sure that one is measuring the conductivity or electrical resistance of the material itself.

I have taken hundreds of observations, and I have not known any case in plotting a resistance curve against temperature where there is not some kind of an inflection when there occurs any chemical or physical change in the material measured.

Suppose you had the arrangement I have described down in a furnace, and had a means of measuring the temperature, and were measuring the electrical resistance. When you got a violent chemical reaction, you would have unquestionably a decided inflection in the curve. Unfortunately, in my work I did not carry my temperatures on magnesium oxide high enough to get the violent reaction, but as far as I went I can assure you that the figures I have put down, for this class of work, are quite accurate, and they have some bearing on the properties of magnesium oxide. I will put the figures down, temperature against resistivity of MgO in ohms per centimeter cube.

C°	Resistivity in ohms per centimeter cube
1060	420,000
1100	320,000
1170	62,000
1230	24,000
1352	510
1386	415

I should say, to be accurate, that there was mixed with the magnesium oxide 10 percent of pure magnesium carbonate. The presence of this amount of magnesium carbonate seemed to slightly cake or sinter the electrically shrunk magnesium oxide, so that the mixture did not drop out from between the slabs of graphite. It is, after heating, about as hard as plaster of paris.

The figures just given by themselves are not so interesting unless you have some comparison figures. I give now some figures obtained for electrically shrunk aluminum oxide. It was in the form of powder, and is as pure as the best made by the

Norton Company. I only list here every fifth one of the figures I obtained:

C°	Ohms per centimeter cube
26	90×10^6
1170	23.8×10^3
1380	16.3×10^3
1458	6.5×10^3

Noting the above figures, we have 16,300 ohms as the resistivity of Al_2O_3 against 415 ohms as the resistivity of MgO at a temperature of 1,380° C. Now why this difference? Perhaps the following fact has some bearing. When I took apart the graphite slabs between which the MgO had been clamped, their surfaces were covered with a thin blackish deposit of what appeared to be amorphous carbon, but when I took apart the graphite slabs between which the Al_2O_3 had been clamped the surfaces were polished, clean, and unaltered in appearance. It seems certain therefore that at a temperature of 1,450° C. there is no reaction between aluminum oxide and graphite, and that there is a slight reaction between magnesium oxide and graphite.

Without making any measurements of resistance or temperature I heated the magnesium oxide considerably higher than 1,450° C. and noted that the resistance went on falling rapidly and that it becomes unfit for an electrical insulator between slabs of graphite when the temperature is very high. By a small increase of voltage an arc is established at these high temperatures, which breaks the insulation down completely.

I think if some one interested in studying chemical reactions at these high temperatures would use the method I have suggested and plot resistivity curves, they would learn from the inflections in the curves where reactions begin and obtain perhaps some idea of their violence. The measurements should be made with low frequency alternating current—low frequency rather than high because there seem to be some strange capacity effects—and an alternating current galvanometer or sensitive electrodynamometer should be used as a detector. An ordinary Wheatstone-bridge connection should be used. It is probable that chemical changes would be shown by marked inflections in the curve. It would not be difficult to arrange for measuring the temperature. A graphite tube closed at the lower end could be inserted

in the furnace and the bottom of this tube could then be viewed with an optical pyrometer. No fumes coming from the furnace could enter the tube to obscure the view.

Many ideas are held as to what constitutes high temperature; but I do not call a temperature high until one has passed 1,000° C. I wish more people would get busy on lines of investigation above 1,000° C., as it is the most fruitful field for original research work I know of.

A. T. HINCKLEY: I would like to point out a case in which the temperature of reaction between carbon and magnesia (MgO) is lower than that given in this paper.

Petroleum coke (ash under 0.5 percent and volatile matter under 0.25 percent) was finely ground and mixed with pulverized magnesia. This mixture was bonded with tar, molded and then baked to remove the volatile matter. This test piece was heated in a carbon tube furnace and the temperatures noted by means of Seger cones. At about 1,500° C. a marked decrease occurred in the crushing strength of the test pieces, indicating that the reaction had started, and at 1,600° the vigor of the reaction was marked by deposits on the walls of the tube, as noted by other workers.

The results indicate that the temperature at which this reaction may be termed vigorous depends upon the physical subdivision of the reacting materials and the intimacy of their mixture. On this account it does not seem that the temperature of reaction is well enough fixed to be made a standard for pyrometric measurements.

F. A. J. FITZGERALD: It would be better not to make measurements of "reaction temperatures" until a reaction temperature is defined. As Mr. Hinckley pointed out the so-called reaction temperature depends so closely on the conditions of the experiment that these results have no particular value.

W. R. WHITNEY: I take exception to Mr. Bennett's statement that it would have been better to try this experiment on magnesia fire-brick. A magnesia fire-brick is an indefinite thing, while pure magnesia is definite. We of this Society should stand for the knowledge gained from what we test, and when a man says he has tested a thing, we want to know exactly what he tested.

Moissan, in his book, mentions the fact that plates of magnesia in contact with carbon are stable at arc temperatures, and he used blocks of magnesia against blocks of carbon in the arc furnace. Therefore it must be an important matter to have the magnesia and the carbon in very close contact to produce any very violent reaction at 2,000° C.

J. W. RICHARDS: Whether a reaction between magnesia and carbon will take place at a given temperature will depend on the pressure put upon them. If the two are strongly compressed they will react at a lower temperature than if they are simply lying against each other. It also depends on the intimacy with which the materials are mixed.

What is the "temperature of reaction" is also indefinite, because in these reversible reactions the velocity of the reaction, starting low at a low temperature, increases very rapidly in a certain region of temperature, and it is only that range of temperature which can be indicated, and not any definite temperature, as one of active reaction. The practical temperatures at which endothermic reductions take place are roughly proportional to the amount of heat absorbed in the reaction. This is only another way of saying that the stronger the oxide the higher the temperature necessary to reduce it by carbon. The data to prove this generalization are fragmentary, but may be illustrated by the following approximate figures:

Oxide reduced	Calories absorbed per atom of oxygen	Approx. Temperature for Reduction
PbO	21,500	500° C.
FeO	36,500	750° C.
SnO_2	41,500	900° C.
ZnO	55,500	1050° C.
SiO_2	69,000	1500° C.
TiO_2	80,000	1600° C.
Al_2O_3	101,500	1800° C.
MgO	114,000	1950° C.

This is only a crude statement of a difficult problem, but it has its applications. Another deduction from these principles is that at any given reduction temperature, with several oxides present, the relative amounts of each reduced will be governed by the same considerations, and may be predicted from the calories absorbed in each reduction. An example of this is the presence of considerable silicon, some titanium and sometimes

traces of aluminium in pig iron produced in the blast furnace. There are no large or important exceptions to this general principle.

WILLIAM R. MOTT: Referring to what Dr. Whitney said about Moissan's work, it is interesting to recall that Moissan tested several kinds of magnesia. He says that the magnesia purified by the method of Schloesing was not reduced by carbon. (See Moissan's book, The Electric Furnace, Translation by Lenher, page 24. Schloesing, C. R.) Moissan showed that the density of magnesia changed from 3.19 to 3.65 on heating in the electric furnace. Along with this change in density, Horton has found a peculiar change in resistance. (Magnesia decreased rapidly in resistance to about 1,200° C. but at 1,300° C. increases in resistance.) Hence, Prof. Kowalke is asked to discuss the effect of using magnesia of different densities on temperature of reaction, as well as magnesia prepared in different chemical ways.

W. R. WHITNEY: I would ask Prof. Northrup whether the small variation in figures for alumina depends on its purity, because in electrical conductivity the question of impurity is very important. Would impure alumina depart very much from that?

E. F. NORTHRUP: I measured alundum, which has a binder in it, and it has a little less resistance. Your question brings up an extremely important point that must be considered in these high temperature measurements. Suppose you had water between two electrodes in a vessel, and the vessel was filled with sand, and you were to pass current between the electrodes, you would have no idea of the electrical conductivity of the sand, for you would be electrically measuring not the sand but the water. When you bring these oxides to these high temperatures, the pores or interstices of the oxides are filled, in all my measurements, at least, with a mixture of other things; nitrogen, CO and free carbon. When you get over 1,500° C. there is always some free carbon vapor, and you measure the conductance of the oxide itself, in parallel with the conductance of the gas, which is by no means insignificant.

Alumina has a resistivity of 40 at 1,550° C. The same space filled with nothing but CO gas has an electrical resistivity of 8.5 at the same temperature. So a great deal of the conductivity

is due to the conductivity of the gas in the interstices of the material, and when one reaches these high temperatures, this has to be taken into consideration. You are not measuring the conductivity of the material itself, you are measuring the conductivity of the material plus the conductivity of the gas. It is not a question of a current which will go through a galvanometer, but it is a question of several milli-amperes which will pass through the gas.

President Lidbury: These magnesia figures you gave, you stated were not for pure magnesia, but a mixture?

E. F. Northrup: Ten percent admixture of magnesium carbonate.

President Lidbury: That might have had some influence on the kinks?

E. F. Northrup: I do not think that had any great effect in bringing the resistance down. It was magnesia, plus 10 percent of pure magnesium carbonate.

K. H. Hitchcock: A good many years ago I tried the best Greek magnesite brick I could get as retainer for a granular carbon resistor in an electric furnace, of that type where the resistor surrounded the glass bath, and I found that at a temperature in the resistor sufficient to liquify the glass in the bath, the magnesite did react with the carbon.

I am not familiar with the experiments of Moissan to which allusion has been made, but in the ordinary arc furnace the magnesite would not come in direct contact with the incandescent carbon, but with either the vapor of carbon, CO or CO_2, or more accurately a mixture of all these gases, which would greatly affect the reaction to which the magnesite itself would be subjected.

There is another thing about the magnesite brick in connection with the resistor furnace above alluded to: It was noticed when any reaction started at a given point in the resistor, the resistor failed with considerable rapidity, and that these failures were never general, along the whole line of the resistor, but more violent in one particular spot.

FRANCIS C. FRARY: I would like to point out one other point: the possibility of an explanation of the volatilization of MgO. It is suggested this volatilized as magnesia and as carbide. I shall show in a paper which is to be read tomorrow[1] that there is a sub-oxide of magnesium which is formed by the reduction of magnesium oxide at temperatures below 1,000 degrees. It is probable that it would have a different volatility and different properties from either of the other substances, and might account for the phenomena observed.

L. E. SAUNDERS: I think attention should be drawn to the fact that magnesium oxide has a considerable vapor tension below the temperatures which the authors of this paper have described; for instance, at 1,700 or 1,800° C. vapors of magnesium oxide will be given off when there is no contact with carbon at all, and probably carbon also has an appreciable vapor tension at the same temperature. That might account for some of the reaction products which the authors describe, accounting for them in another way.

I would call attention to the fact that the authors of the paper state that the materials used in the reactions were the purest attainable. That is rather a presumptuous statement.

[1] See page 209.

A paper presented at the Twenty-seventh General Meeting of the American Electrochemical Society, at Atlantic City, N. J., April 23, 1915, President F. A. Lidbury in the Chair.

THE THERMO-ELECTROMOTIVE FORCE OF CERTAIN IRON ALLOYS

By T. S. Fuller.

Much work has been done in the past on the thermo-electromotive force of the pure metals, and alloys of the noble metals. Comparatively few measurements, however, have been made on base-metal alloys. Euchen and Gehlhoff[1] have measured the thermo-electromotive force of the antimony-cadmium series; M. R. Ledoux[2] has measured the copper-tin series; K. E. F. Schmidt[3] has taken up the discussion of the thermo-electromotive force of copper-nickel alloys measured against manganin, and of the iron-nickel alloys measured against manganin, iron and platinum, and W. Broniewski[4] takes up the discussion of the following systems—Au-Ag, Cu-Ni, Bi-Sb, Ag-Pt, Ag-Pd, Pt-Rh, Pt-Ir, Bi-Pb, Bi-Cd, Bi-Sn, Cu-Co, Cd-Sb, Cu-Al.

The phenomenon of thermo-electromotive force was first observed by Seebeck in 1821. He gave the name thermo-electric to the current produced to distinguish it from the ordinary voltaic or hydro-electric current.

If small pieces of two dissimilar metals are welded together at one end, while the other ends are connected through a galvanometer, and if the junction is heated, a current will flow, the direction of which will be indicated by the deflection of the galvanometer. If, however, the junction is cooled by immersing in a salt solution, a current will be produced in a direction opposite to the former, as will be shown by the deflection of the galvanometer. The strength of the current calculated from the deflection is found to be proportional to the electromotive force of the thermo-element.

[1] Ber. deut. Phys. Ges., **14**, 169-182 (1912).
[2] Compt. rend., **155**, 35 (1912).
[3] Phys. Z., **10**, 438-45 (1909).
[4] Rev. Metal., **7**, 341-67.

The thermo-electromotive force of all of the common metals has been determined with respect to a standard (usually platinum) and formed into a thermo-electric series with bismuth the most highly negative and antimony the most highly positive. (Kaye and Laby, Physical and Chemical Constants, p. 47, 1911.)

Method of Making the Alloys.

Most of the alloys used in this investigation were melted either in an atmosphere of hydrogen or *in vacuo*. One-hundred-gram slugs were made in alumina crucibles, the melts being thoroughly stirred with a fused quartz rod. The metals used were as follows: Swedish iron, Goldschmidt chromium and manganese, nickel from the International Nickel Company, and cobalt furnished by Eimer and Amend, having a purity of 98-99 percent. The composition of the alloys is given in Tables I-V. Those marked with a * have been analyzed, the others are compositions by addition. The metals added were carefully weighed, and the slug when cool was weighed again. None lost in melting over three or four percent of the total weight.

Preparation of the Couples.

All the measurements in this investigation were made against copper as a standard. Portions of the one hundred gram melts were swaged and drawn down to wire having a diameter of 0.010 in. Each wire was then electrically annealed and arc-welded to a copper wire of the same size. The welded joint of each couple served as the hot junction and was placed inside a glass tube closed at the bottom and immersed in boiling water. The two cold junction ends of the couple were then twisted to copper leads, the junctions placed in glass tubes and immersed in a bath of melting ice.

Measurements.

The thermo-electromotive force of each couple was measured by means of a potentiometer, which consists of a standard resistance, through which a measured and controllable current flows. This instrument was calibrated against a Leeds and Northrup potentiometer. The zero method was used, e. g., the measured current flowing through the standard resistance was regulated

until there was zero deflection of the galvanometer, or in other words, until the *RI* drop across the standard resistance exactly balanced the thermo-electromotive force of the couple under examination.

Results.

The thermo-electromotive force in the tables, following, was measured against copper and is expressed in millivolts. Hot junction = 100° C. Cold junction = 0° C. Current flows across hot junction from metal with algebraically smaller value to other metal.

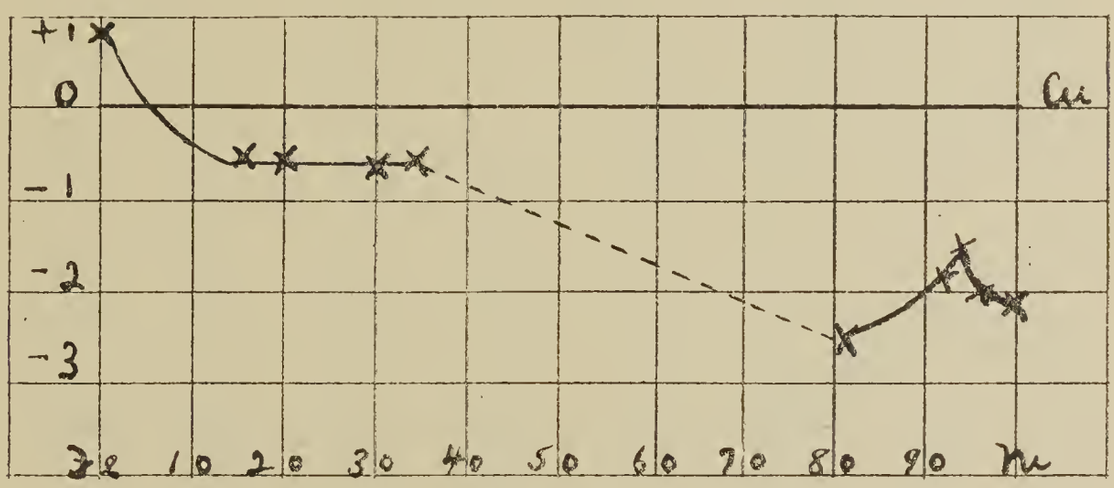


Fig. 1

The curves are drawn from the data in the tables. The thermo-electromotive force expressed in millivolts is plotted against composition for the binary alloys. The zero line represents the copper standard. The distance above this line represents values thermo-electrically positive with respect to copper, and the distance below this line values thermo-electrically negative. The curves for the two series of ternary alloys are plotted on triangular diagrams, the perpendicular distance from the sides representing the proportion of the constituents. The numbers give the thermo-electric value of the respective alloys.

The following values for iron, nickel and copper measured against platinum over the range 0° C.-100° C. are given in Kaye and Laby, Physical and Chemical Constants, p. 47 (1911):

Metal	Millivolts
Iron	+1.600
Copper	+0.740
Nickel	—1.640

Table I.

Thermo-electromotive Force of Iron-nickel Alloys.

(Against Copper. 0 to 100°.)

Fe	Ni	Si	C	T. E. F. Millivolts
100.	.....	.....	.....	+0.86
83.	17.	.....	.....	—0.64
80.	20.	.....	.....	—0.55
70.	30.	.....	.....	—0.52
*66.5	33.5	0.16	0.25	—0.48
*18.8	81.2	0.014	0.19	—2.45
7.	93.	.....	.....	—1.90
*4.6	94.6	0.64	0.11	—1.40
*3.2	96.3	0.35	0.12	—2.00
....	100.	.....	.....	—2.38

* By analysis; the others by addition.

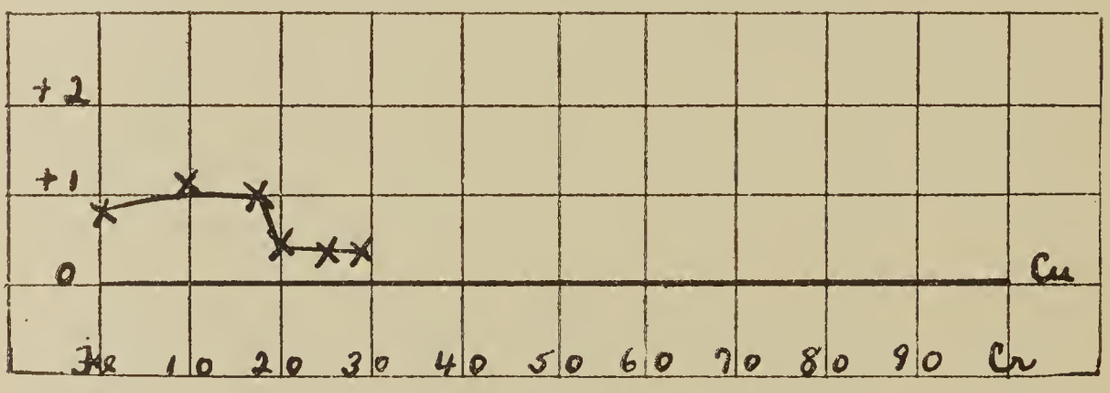


Fig. 2.

Table II.

Thermo-electromotive Force of Iron-chromium Alloys.

(Against Copper. 0 to 100°.)

Fe	Cr	T. E. F. Millivolts
90.	10.	+1.20
82.	18.	+1.04
80.	20.	+0.43
76.5	23.5	+0.32
70.5	29.48	+0.31

Table III.

Thermo-electromotive Force of Iron-cobalt Alloys.

(Against Copper. 0 to 100°.)

Fe	Co	T. E. F. Millivolts
90.	10.	—0.64
80.	20.	—3.70
70.	30.	—3.50

Table IV.

Thermo-electromotive Force of Iron-nickel-chromium Alloys.

(Against Copper. 0 to 100°.)

Fe	Ni	Cr	Mn	Si	C	T. E. F. Millivolts
79.	17.	4.	...	...	...	—0.12
70.	20.	10.	...	...	...	—0.46
35.	55.	10.	...	...	...	+0.00
25.	60.	15.	...	...	...	+0.07
25.	55.	20.	...	...	...	+0.07
20.	55.	25.	...	...	...	—0.08
*17.5	75.5	7.	...	0.03	0.22	+0.20
*16.3	70.6	13.1	...	0.02	0.17	+0.20
*16.3	70.6	13.1	...	0.02	0.20	+0.17
*9.6	57.7	31.9	0.20	0.30	0.40	—0.08
*6.4	69.	22.7	0.30	0.25	0.20	+0.24
*5.	84.	11.	...	0.40	0.034	+1.49
*4.5	81.	13.6	0.30	0.30	0.17	+1.00
4.	89.6	5.65	...	...	...	+1.70
*4.	80.4	15.6	...	0.58	0.23	+0.76
*3.8	89.7	5.6	0.25	0.40	0.18	+1.51

* By analysis; the others by addition.

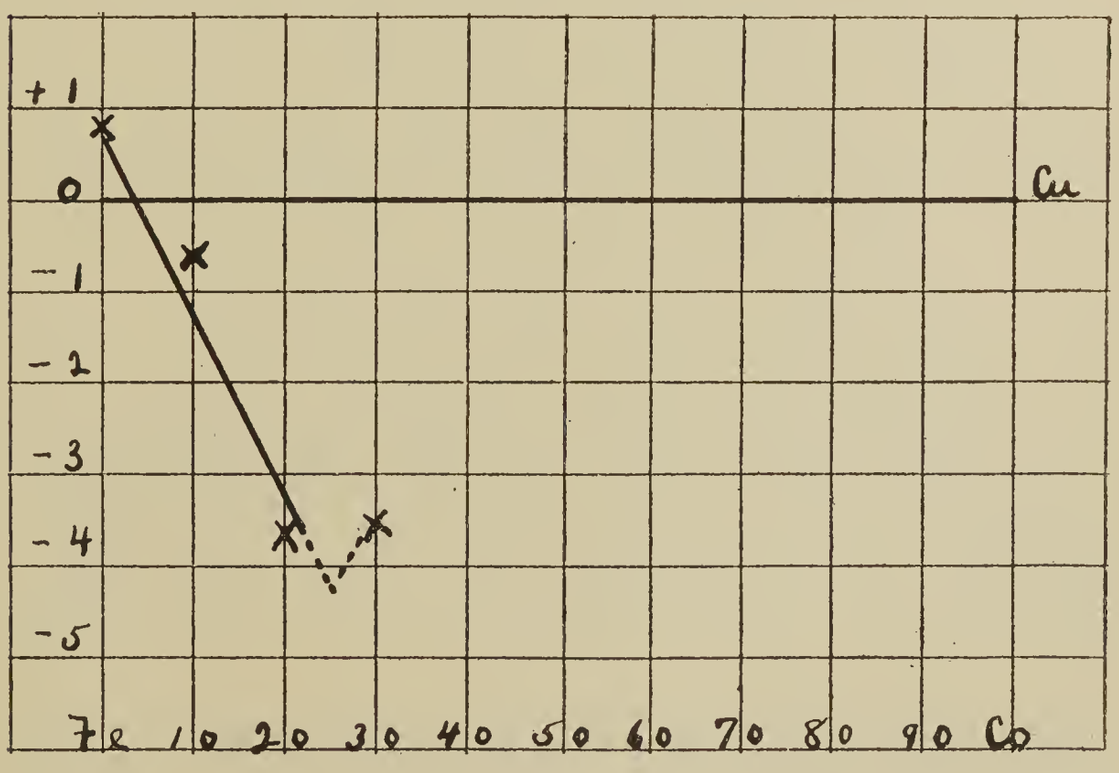


Fig. 3.

Table V.

Thermo-electromotive Force of Iron-nickel-manganese Alloys.

(Against Copper. 0 to 100°.)

Fe	Ni	Cr	Mn	Si	C	T. E. F. Millivolts
87.	10.	...	3.	...	...	—1.09
86.	12.	...	2.	...	...	—1.02
81.	17.	...	2.	...	...	—1.50
80.	17.	...	3.	...	...	—0.79
76.5	17.5	...	6.	...	...	—0.73
76.	22.	...	2.	...	...	—1.84
50.	44.	...	6.	...	...	—0.59
*33.6	58.3	0.31	6.6	1.	0.16	—0.94
*5.	82.8	0.11	12.	0.058	0.068	—1.11
*5.	88.5	0.11	6.2	0.061	0.065	—1.60

* By analysis; the others by addition.

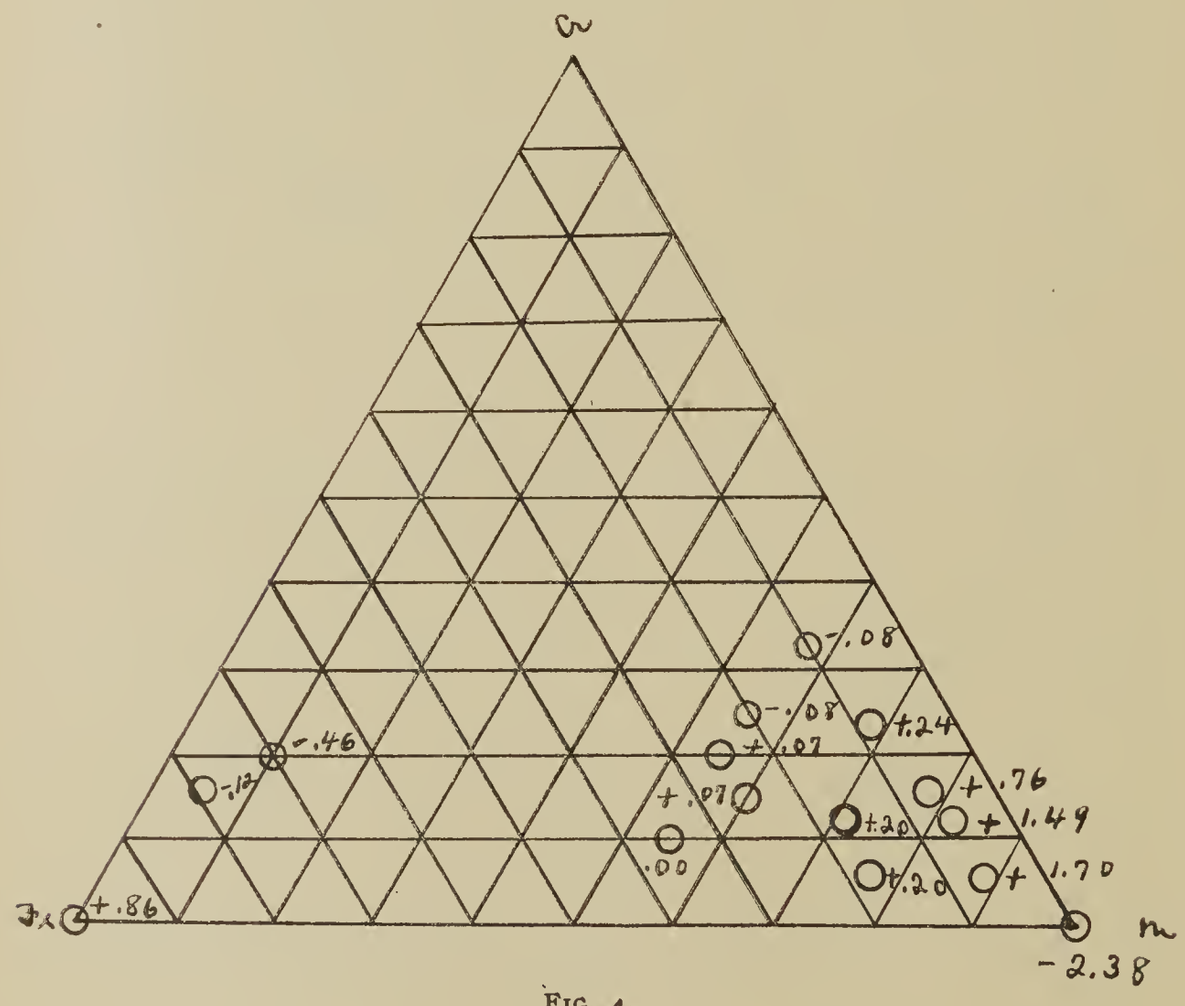


Fig. 4.

Table I and Fig. 1 refer to the iron-nickel series. All of the alloys measured showed negative values. There is apparently

a maximum negative value, somewhat greater than the value for pure nickel, at the composition 81Ni-19Fe, although we cannot be sure of this because of the lack of further points.

Table II and Fig. 2, dealing with a short series of iron-chromium alloys, show all positive values, and show that the change in thermo-electric properties of iron caused by the addition of chromium up to 30 percent is comparatively small.

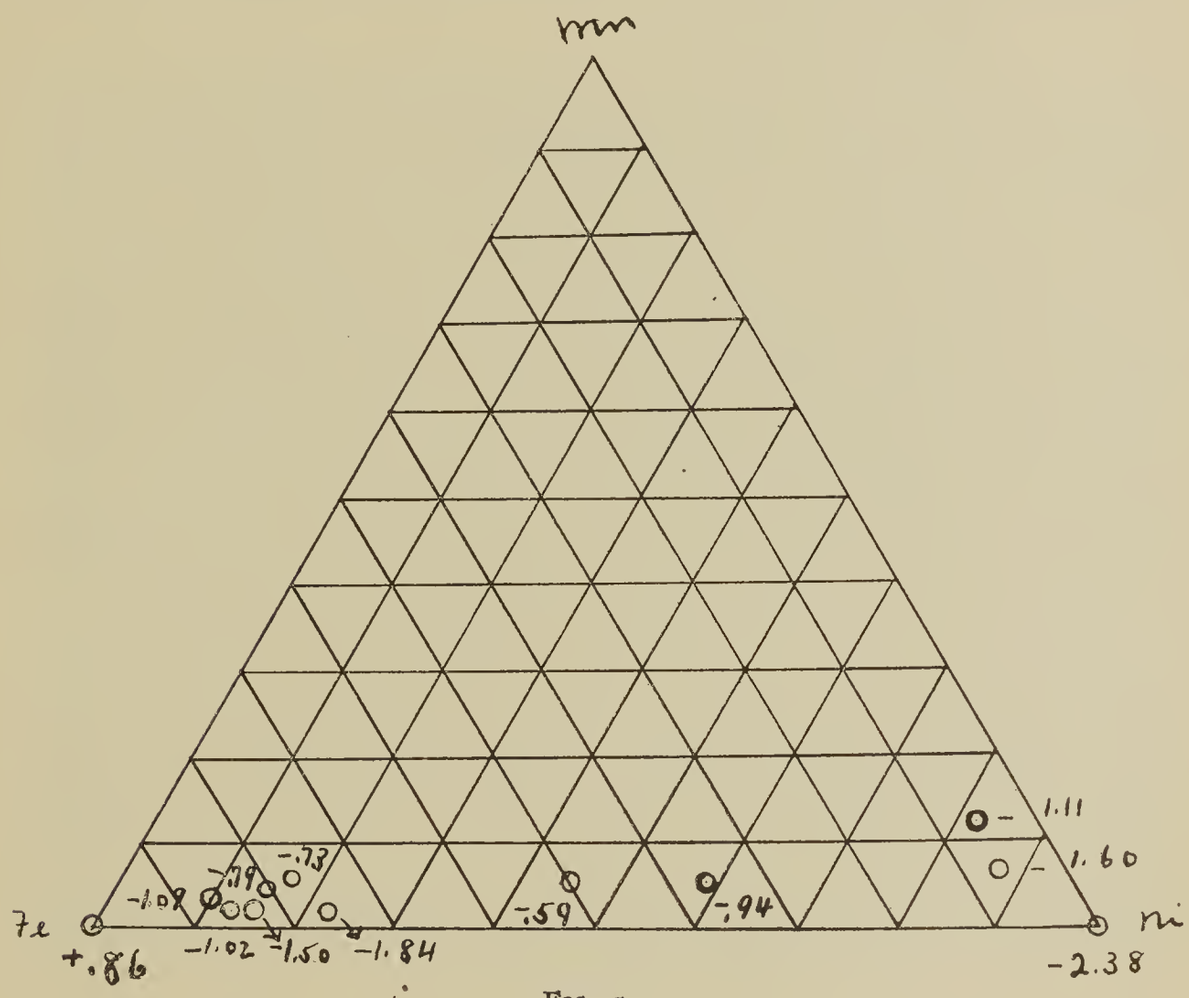


FIG. 5.

Table III and Fig. 3 show that the addition of cobalt to iron has a very marked effect thermo-electrically. The three alloys show negative values. There is a difference of potential between iron and the 20 percent Co-Fe alloy over the range 0° C.-100° C. of 0.86 and —3.70 = 4.56 millivolts. It is probable that there is a maximum negative value between the 20 and 30 percent alloys, but again we cannot be sure of this for lack of further points.

Table IV and Fig. 4 show the iron-nickel-chromium series. The alloys containing 80-90 percent Ni, and the balance iron

and chromium are worthy of note. They have positive thermo-electromotive forces ranging from 1.00 to 1.70 millivolts, while pure nickel has a negative value of —2.38 millivolts.

Table V and Fig. 5 show the iron-nickel-manganese series. All the alloys measured show negative values.

Research Laboratory,
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DISCUSSION.

O. L. Kowalke (*Communicated*): This is a most valuable paper. It would also be useful to have data on the relation between temperature and electromotive force above 100° C. Some metals and alloys show a distinct change in the relation of temperature to electromotive force above 800° C.

Have any tests been made to determine the resistance to oxidation of these alloys at higher temperatures than 100° C.?

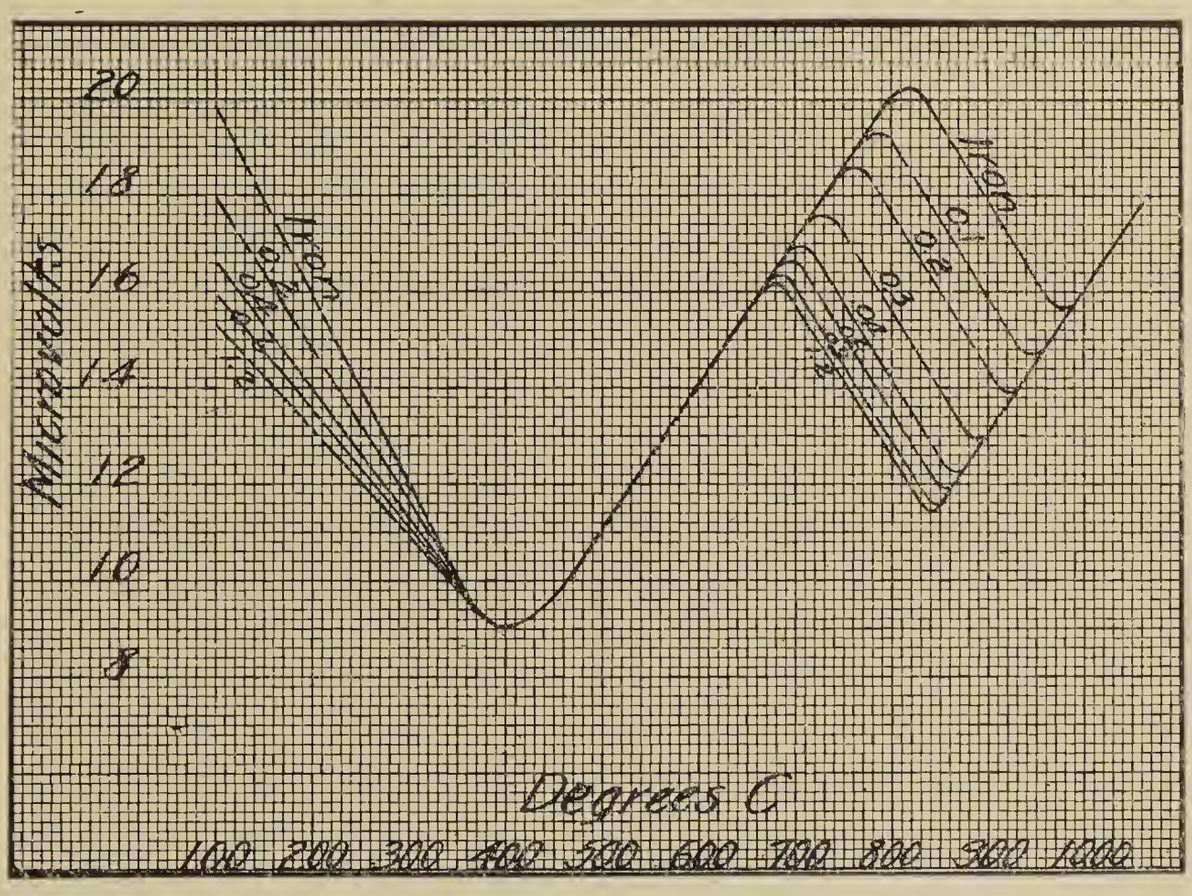
C. G. Fink: I do not believe Mr. Fuller, in presenting his paper, impressed the audience with the amount of work connected with it. I happen to be acquainted with some of Mr. Fuller's work, and I know he has given a great deal of time to this subject.

Has Mr. Fuller noticed any difference in the electromotive force due to varying quantities of sulphur or carbon? On page 244 I see the carbon content varies between 0.1 percent and 0.3 percent. How does the carbon content and the silicon content affect the electromotive force? It certainly affects the electrical resistance, and I am interested in knowing how it affects the thermal electromotive force. I think in all of these measurements we ought to state the amount, and if possible the effect of these impurities.

W. R. Mott: I had in mind the same question on the influence of carbon as that asked by Dr. Fink, and in this connection I call attention to Belloc's work on "Thermo-electricity of Steels" (C. R. (1900) **131**, 336, and (1902) **134**, 105). The phase rela-

tions, recalescence, etc., affect the thermo-electric value. Belloc's diagram is given below, on the thermo-electric relation of iron to percent carbon and temperature.

Burgess and Le Chatelier, in their book (last edition, Measurement of High Temperature, page 103) speak of the difficulty of reproducing results and of variations depending on physical conditions, whether drawn or annealed or what not. They say "These anomalies may sometimes be due to accidental variations



Thermo-electricity of Steels.

in the composition of wires, and a physical heterogeneity due to the heating is produced. Iron and nickel heated respectively to 750° and 380° undergo an allotropic transformation, incompletely reversible by rapid cooling."

Jos. W. Richards: In connection with this equilateral triangular diagram, Mr. Ashley showed (Trans. Am. Inst. Mining Engineers, 1901) that a rectangular diagram could be constructed inside a 45° right-angled triangle, wherein x (abscissas) represents one constituent, up to 100, y (ordinates) represents another constituent, up to 100. Draw a line from x = 100 to y = 100,

forming thus the hypothenuse of a 45° right-angled triangle. Then for any point in the triangle, x is one constituent, y is another, and the vertical (or horizontal) distance to the hypothenuse represents the third, assuming the sum of the three constituents constant.

To my mind, and in my experience, this is a far better method than using co-ordinates at 60°, because we are all accustomed to rectangular co-ordinates, and the diagram is quite as clear and usable one way as the other.

The industrial usefulness of these two thermo-electric couples depends on their resistance to oxidation at high temperatures, and, therefore, when they come to be compared, their resistance to oxidation should be studied in connection with the paper which is to come up this afternoon on calorizing metals. Might it not be practicable and industrially valuable to calorize these wires, if that could be done, to protect them from oxidation and thus lengthen their lives?

Francis C. Frary: There is another method of plotting a three component system on rectangular co-ordinates; which is very convenient in many cases, and that is to take one component and assume it to be the solvent for the other two, and plot these two against one another, in grams against per hundred grams of the solvent. In this case you might assume the iron to be the solvent, and you plot the nickel, the chromium, the nickel in grams per hundred grams iron, and the chromium in the same units, and you get a curve. For different proportions of carbon, if you want to get four components on a rectangular system, you can draw the different curves on the same scheme and get something which sometimes is a little bit more obvious and more useful to work with than triangular co-ordinates.

A. T. Hinckley: I wish to ask if the effect of heat-treating these alloys has been studied. We find that the crystallization of base metal couples caused by successive heating and cooling is one of their most serious faults.

H. C. Chapin: What Prof. Richards said about calorizing these wires would be valuable if it could be done, but would it be possible in consideration of the fact that the aluminum penetrates slightly to the center of the material, according to Mr.

Ruder's paper, so there would be actually a change in the structure of the wire, something more than the mere protection of the surface.

W. E. RUDER: Suppose we leave the question of calorizing until this afternoon. That matter will come up in the regular course. (See discussion of paper by W. E. Ruder, page 262.)

T. S. FULLER (*Communicated*): Referring to Dr. Fink's question about the effect of carbon and silicon on the thermo-electric properties of these alloys, I am sorry that I have no data. I would, however, refer him to an article by Broniewski, on The Thermo-electromotive Force of Steels (C. R. (1913) **156**, 1983-85). Here measurements were made on steels of 0.07, 0.24, 0.44, 0.79, and 1.12 carbon content.

I was rather surprised at Mr. Mott speaking of the difference between the thermo-electric properties of hard-drawn and annealed wires. In the samples that we have tested we have never found the annealed and unannealed wires to vary over two or three percent. Mr. Mott quotes from "High Temperature Measurements," by Burgess and Le Chatelier, and speaks of the difficulty of reproducing results. It seems to me that the composition, the method of making the alloys and the method of annealing, determine largely whether or not the results may be reproduced. We have never had any trouble in checking results. We surely do intend to continue this work by making measurements at higher temperatures.

We have not measured the thermo-electromotive force of any wires that have been heated to a high temperature long enough to crystallize. These measurements were all made on samples which were annealed by passing an electric current through the wire for perhaps fifteen seconds. None of them were heated long enough to have a chance to crystallize to any extent.

A paper presented at the Twenty-seventh General Meeting of the American Electrochemical Society, at Atlantic City, N. J., April 23, 1915, President F. A. Lidbury in the Chair.

CALORIZING METALS

By W. E. Ruder.

There are numerous processes of manufacture, especially in metallurgical lines, which require the use of metal containers and parts which will withstand oxidation at temperatures above red heat. There is no metal which will fill this requirement that is cheap enough for general use. There are some alloys, usually rich in chromium or nickel, which are fairly good resistors of oxidation, but these are either too expensive or offer too great a difficulty in mechanical working, and so have not come into general use in structural work.

Iron and steel are used for most high temperature work, because of their low cost and adaptability, but the parts have to be frequently renewed if they are subject to oxidizing conditions. Nickel has a higher oxidizing point but is too expensive for ordinary use.

According to F. Robin (Bl. Soc. Eng. (1912) 222) steel begins to burn at 370° C., Ni at 660° C., German silver at 500° C., Cu at 360° C., Ni 90-Cr 10 at 650° C., Al bronze (9.2 percent Al) at 600 and Ni steel (58 percent Ni) at 530° C. There is no great amount of burning in steel and iron, however, until a temperature of 500° C. is attained, but above this point the oxidation is very rapid. Likewise, Ni, although it begins to increase in weight at 660° C. is not seriously affected until a considerably higher temperature is attained.

Allison and Hawkins, in a recent paper (cf. G. E. Rev. 1914, **17**, 947) describe a process for the protection of metals at high temperatures. This process, called "calorizing," consists in producing a rich aluminum alloy upon the surface of the metal to be protected. It is the purpose of this paper to give the results of a study of the application of this process to various metals.

The process as used at present consists briefly in packing the pieces in a mixture containing powdered aluminum. This mixture is made up of alumina and powdered aluminum with the addition of about 1 percent of ammonium chloride. The aluminum varies from 5 percent to 50 percent by weight, depending upon the service to which the piece is to be put. For copper and brass parts the mixture is kept low in aluminum and the

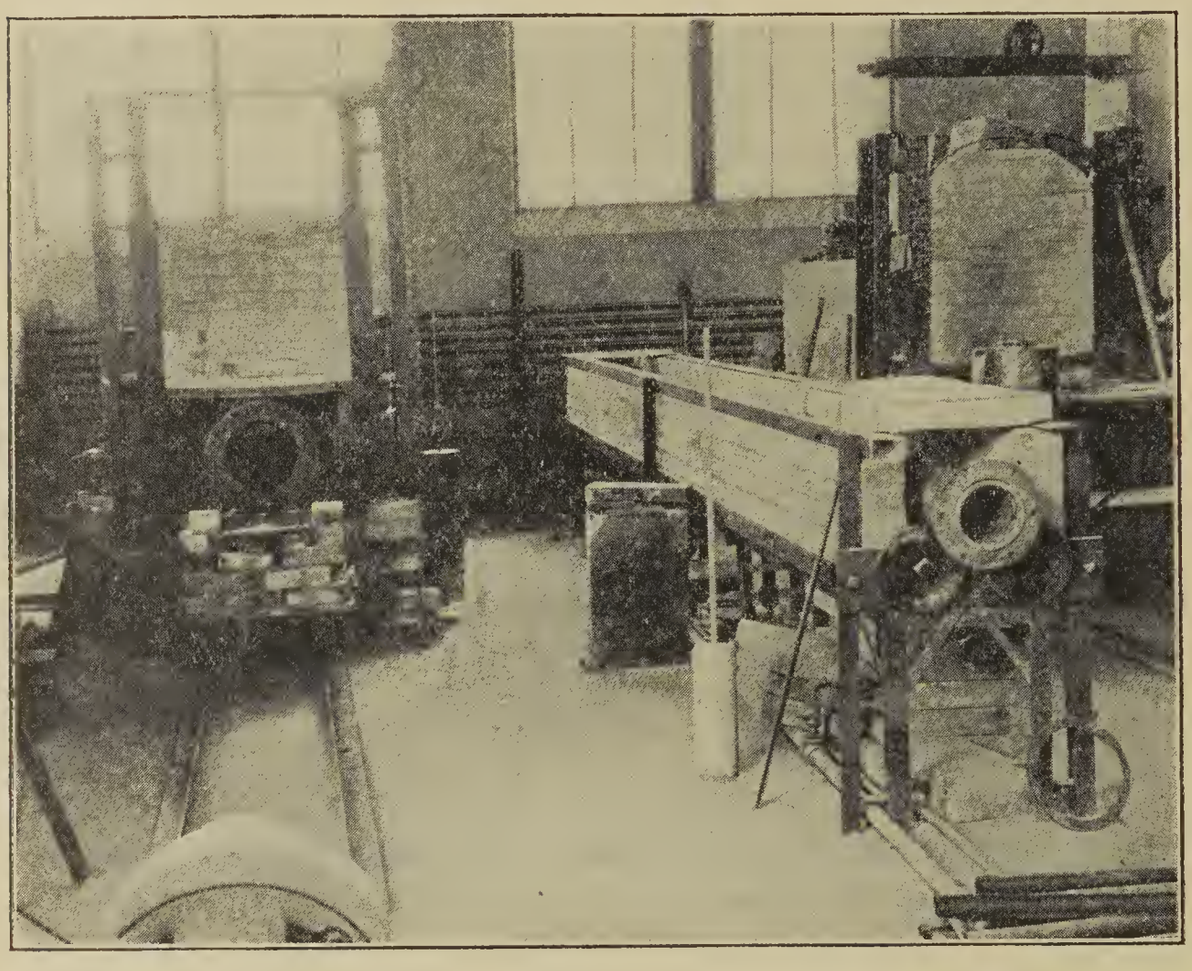


Fig. 1.

temperature of firing held at about 700° C.-800° C. For steel and iron, richer mixtures are used and the temperature of firing is increased to 900-950° C. These mixtures are used repeatedly with the addition of sufficient aluminum and ammonium chloride to make up for the loss at each firing.

The pieces to be calorized are packed in this mixture in a gas-tight receptacle which is filled with a reducing or inert gas to prevent the burning of the aluminum and slowly brought up to temperature. The time of firing also depends upon the

depth of coating required, but usually 2-3 hours is found sufficient for most purposes.

The process is not unlike the cementation process in that the result is not a coating of aluminum but an absorption of aluminum by the metal to form an alloy. The furnaces used are

Fig. 2.

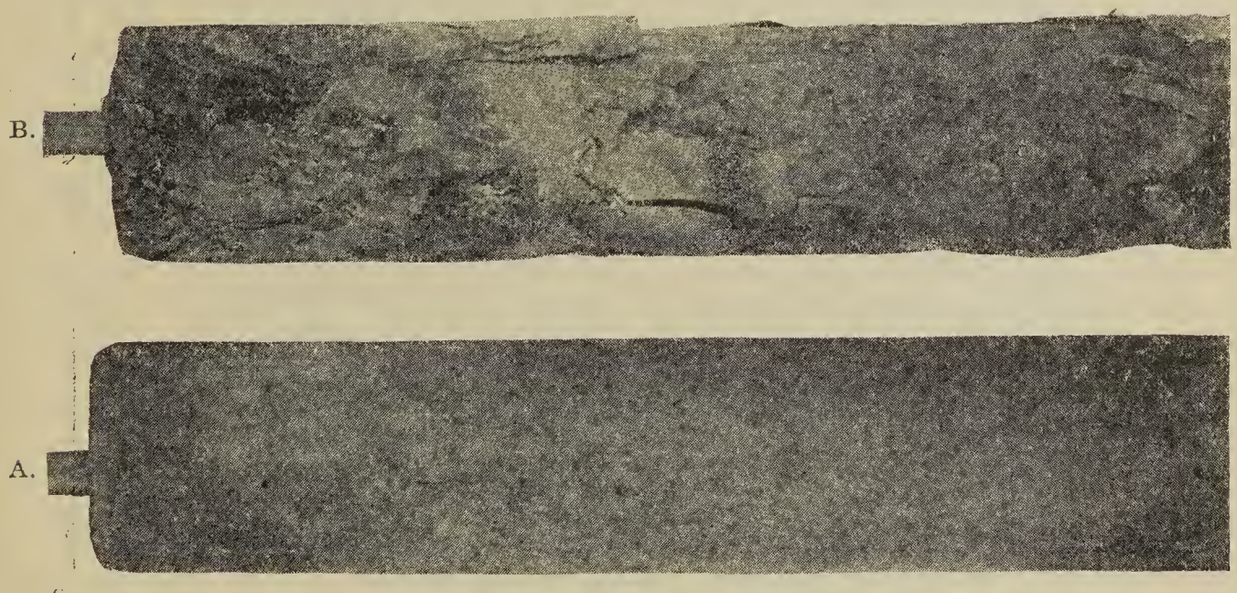


Fig. 3.

shown in Fig. 1. These are gas-fired, and so built that receptacles of odd shapes and sizes may be fired to any desired temperature. The long furnace is particularly for the treatment of tubes.

Perhaps the most important application of this process is in the treatment of iron to withstand high temperatures. The speci-

mens shown in Figs. 2 and 3 are of (a) calorized and (b) uncalorized iron tubing. These were all heated in an open flame, under the same conditions, to a temperature of 900° C. for a total of 8 hours. At the end of this time the tubes (a) were practically unchanged with the exception of a slight surface discoloration, while tubes (b) were scaled and cracked about half way through.

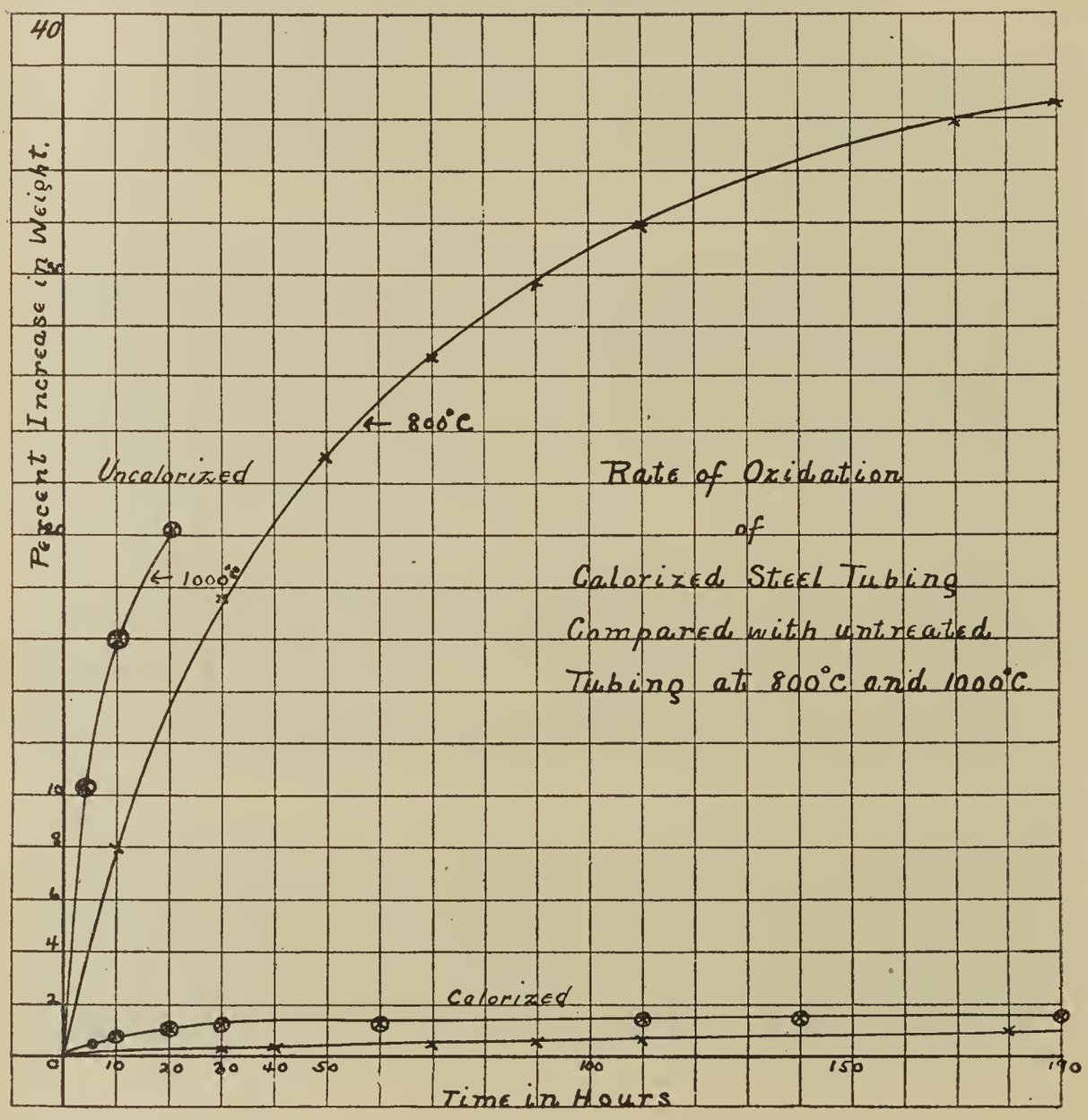


FIG. 4.

The curve shown in Fig. 4 gives the percentage gained in weight by samples fired in air in a resistance furnace to 800° C. and 1000° C. respectively. After twenty hours at 1000° C., the uncalorized piece scaled so badly that it was impossible to carry the curve any further. The calorized samples, after the first

slight gain continued practically unchanged for 500 hours which was the limit of this particular experiment.

When the coating is first put on it is only about 0.001-0.004 inch (0.025 to 0.010 mm.) thick. This coating consists of an

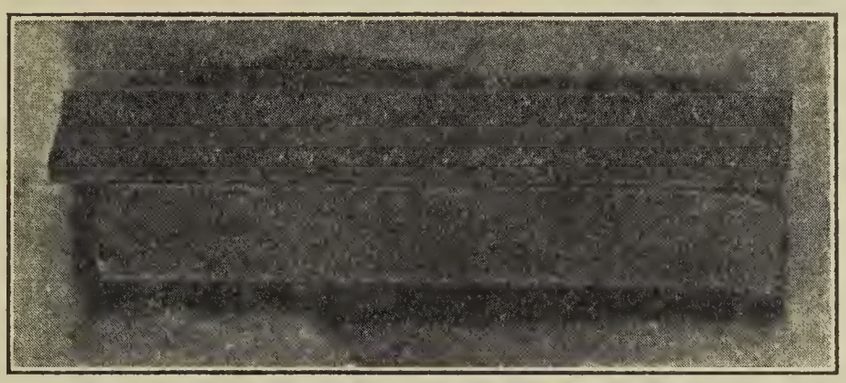


FIG. 5. × 2½

FIG. 5a. × 65

alloy very rich in aluminum. When the piece is kept at a high temperature, as in service, this narrow band of alloy gradually widens as the aluminum diffuses into the iron. This diffusion, which proceeds very slowly at 800-900° C., becomes much more

Fig. 6. × 9

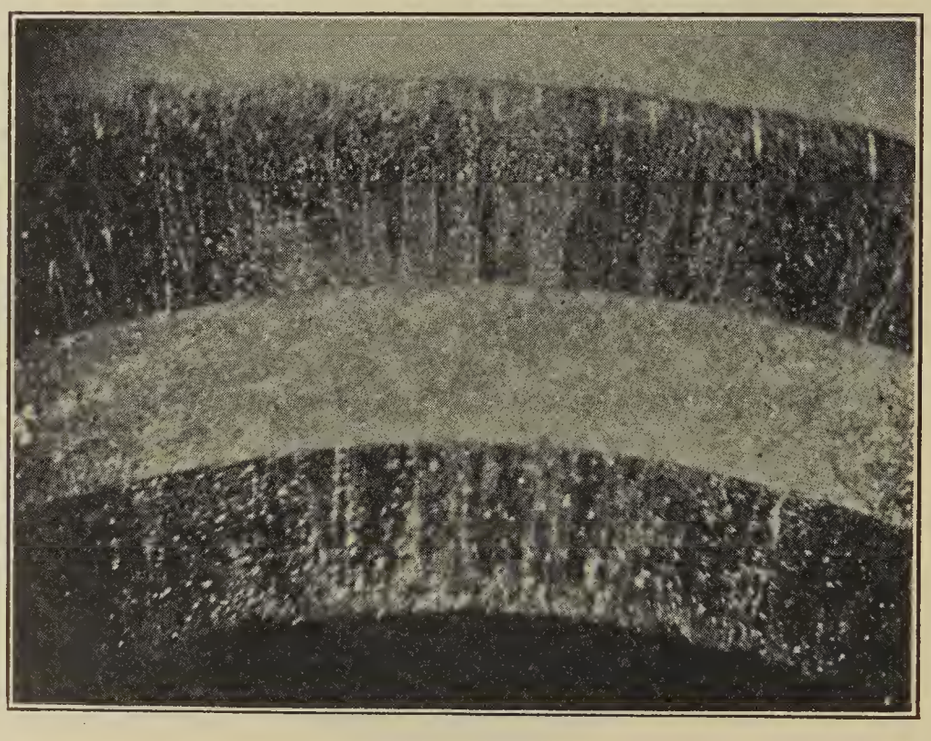


Fig. 7. × 15

rapid with increasing temperature and necessitates the application of a heavy coating of very rich alloy if the piece is to be used at temperatures above 950-1000° C. Fig. 5 (2.5 diameters) shows samples of steel plate as calorized. Fig. 5a shows

the same sample at a magnification of 65 diameters. Fig. 6 (9 diameters) shows the same section after running at 1300° C. for 12 hours. Fig. 7 (15 diameters) shows the section of a tube after running for about 100 hours at 1100° C.

This diffusion gradually lowers the amount of aluminum in the outside coating, especially if the piece be of heavy section. There is, however, a coating of Al_2O_3 all over the outside which still protects the pieces from oxidation, but if this is broken it cannot renew itself and deterioration sets in. This usually starts

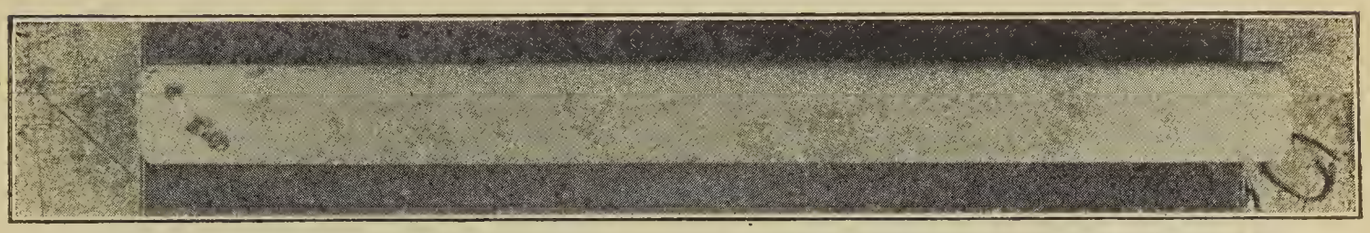


Fig. 8.

Fig. 9. × 12

in spots as shown in Fig. 8, but once started spreads rapidly over the whole surface as a kind of aluminous slag. This spotting, however, occurs only at temperatures above 1050-1100° C., and may be prevented by using a small section so that the alloy when completely diffused still remains high in aluminum. Fig. 9 is the section of such tube (12 diameters) and this tube will run indefinitely at 1100° C. Deterioration may also be started by the contact of Fe_3O_4 with the outside of the tube while hot. This also starts slagging, which spreads rapidly.

Calorized cast iron parts do not stand up quite as well at high temperatures as calorized wrought iron or steel parts, because of the large amount of gases they contain and also because of their tendency to swell. At 800-900° C., however, it stands up very well. Wires and thin ribbons can only be given a light coating if they are to be kept pliable, because the surface alloy is very brittle and, unless very thin, will check off.

This process is finding considerable application in furnace parts, pyrometer tubes, annealing boxes, combustion tubes, etc. The original dimensions are somewhat increased by calorizing,

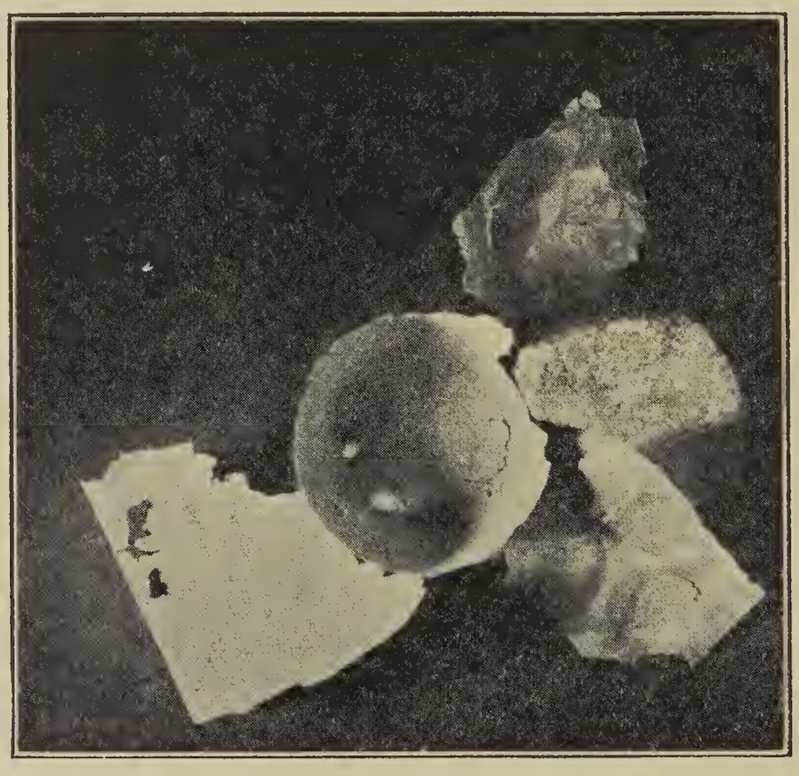


Fig. 10.

especially on the edges. On flat surfaces, however, there is only a very slight increase (0.002-0.004 inch = 0.05 to 0.1 mm.).

Copper parts are equally well protected by calorizing. The result in this case is to produce a coating of aluminum bronze very rich in aluminum. This coating protects the copper from oxidation right up to its melting point. Fig. 10 is a photograph of a calorized copper crucible which has been melted. The Cu has run out leaving the protective shell unchanged. Calorized copper condenser tubes are giving exceptional service.

Nickel may also be calorized. Fig. 11 shows strips of pure Ni which have been fired in the same furnace at 1200° C. for

48 hours. *a* and *b* were calorized, *c* and *d* uncalorized. The uncalorized pieces after this treatment were heavily scaled and brittle, while the calorized samples were unchanged. Calorized nickel is particularly good to use in wire form because the coating, unlike that on iron, is not brittle. Thin ribbons for resistance furnaces, etc., when calorized remain quite pliable. Iron ribbon, on the other hand, becomes very brittle and must be shaped before calorizing or else shaped hot afterwards. Calorized Ni gauze is found to be very durable for combustion screens, etc., as it does not burn and remains pliable.

FIG. 11.

In conclusion it may be said that calorizing protects metals from oxidation indefinitely at temperatures below 1000° C. Above this temperature it still increases the life of metal parts several fold. It is to be noted, however, that it forms no protection against ordinary atmospheric corrosion, except in the case of copper. The aluminum bronze formed in this case is also protective against corrosion.

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DISCUSSION.

LAWRENCE ADDICKS: I notice in the first paragraph that Mr. Ruder speaks about the absence of any competition along this line, that is, that there is no cheap material for construction. It occurs to me that we may not be doing all we could with magnetite for work of that sort. If my memory serves me all right, that is what we have in the ordinary blued steel. In that case the film is so thin that it is probable that the surface would not resist severe oxidation. On the other hand, take these magnetite anodes we were speaking of this morning, where they resisted the most severe oxidation from oxygen formed at the anode itself. It is probably difficult to form a coating of any thickness in practice. Basic copper converters are coated inside with magnetite by blowing a charge of matte without adding silica to flux the ferrous oxide formed. We have a very thick coating there. Something along the same lines may be tried by forming a coating of magnetite on the iron itself. It will not stand the high temperature shown here, but will stand above a red heat.

A. T. HINCKLEY: Is it possible to calorize an iron object which is too large to be packed conveniently in a container? If so, what is a good liquid medium to use in applying the calorizing mixture to the surface of the iron and with what material should this be protected while heating to the temperature required?

F. A. J. FITZGERALD: Has Mr. Ruder made any experiments at all on calorizing the copper parts used in electric furnaces? Sometimes in the case of bus bars, going to an electric furnace, there is a fairly high temperature and a considerable amount of sulphur gas, and you are troubled very much with scale. Could calorizing be used to protect the copper in such places?

WM. R. MOTT: Have you applied this method to soldering irons exposed to the usual soldering fluids containing chlorides? If so, how much is their life increased?

In regard to the exceptionally protective action of aluminum, it is interesting to examine the relation between the volume of the metal in the free condition and in the oxide formed. If these volumes are the same there will tend to be less mechanical breaking of the film in the process of its formation and the film will be more impervious to penetration of gases. In the case

of iron, protective films of magnetite Fe_3O_4 have been tried with varying success, but here the expansion is such as to double the volume and hence to tend to cause a porous structure. Aluminum is one of the metals which expands the least in oxidizing. Zirconium comes close to it in the protective action of its oxide. The following table is given to show the favorable position of aluminum in this respect.

	Sp. Gr.		Sp. Gr.	Volume Increase Percent.
Al	2.6	Al_2O_3	4.0	20
Be	1.7	BeO	3.1	50
Zr	6.4?	ZrO_2	5.7	50 or less
Zn	7.0	ZnO	5.7	54
V	5.5	V_2O_3	4.7	70
Cr	6.9	Cr_2O_3	5.0	100
Fe	7.8	Fe_3O_4	5.2	100

Iron doubles in volume in forming magnetite, and hence same breaks off in the process.

Jos. W. Richards: There is another phenomenon in line with Mr. Mott's explanation. If you take an aluminium wire and heat it to redness by an electric current, suspended between two points, it will oxidize rapidly, but the coating of oxide formed is so tough that the wire does not break and will continue suspended, although the metal in the center of the wire is fluid. When you break open the wire you find a shell of alumina, and some unoxidized aluminium in the center. The continuity of the oxide film is the real reason for the superficial oxidation.

In discussing this process, as well as the sherardizing process, I marvel at the wonderful results which are obtained at the extremely low vapor tensions of the metals. When we were discussing the sherardizing process three years ago,[1] I brought out a calculation of the probable vapor tension of zinc at the sherardizing temperatures, somewhere about 0.01 to 0.05 mm. of mercury, and yet that small pressure is the motive power on which the whole sherardizing process depends. The same calculation can not be made as accurately for aluminium, because its normal boiling point is not so accurately known as that of zinc, but assuming it as 2,250° C. we would have, at the temperature at which Mr. Ruder calorizes iron, a vapor tension about 0.0002 to 0.0005 mm., or approximately one-tenth as great as is used in the sherardizing process with zinc; and at the tem-

[1] Trans. Am. Electrochemical Soc., **21**, 572 (1912).

perature at which he calorizes copper there would be a vapor tension of about 0.0001 mm. of mercury. Undoubtedly these minute vapor tensions are the active and effective agents on which the process depends.

It is very unfortunate that we do not have data about the boiling points of the metals, so that we can construct their curves of vapor tension, and know what the vapor tension of the metal is at any temperature at which we may be working. They run down to an extremely small value. The only complete experimental data we have are in the vapor tension curve of mercury. We have also data in regard to zinc at a limited range near its normal boiling point. We have a few scattered data with regard to the other metals, which are open to a good deal of question.

In my opinion, the Bureau of Standards could do no better service for a large part of the metal industry than to give some accurate values of the vapor tension of the metals at different temperatures. I have calculated the vapor tension of zinc at ordinary temperatures as about 0.3×10^{-15} mm. of mercury, and I have no doubt that most of the other metals are somewhat of that same order, or even lower. One very peculiar thing is that the nose can detect the odor of a number of metals, and sometimes the characteristic odor of different metals, yet the vapor tensions at ordinary temperatures are usually 1×10^{-15} mm. or lower.

With a mixture of the metal in powder and inert oxide, such as used by Mr. Ruder, the calorizing may be done at temperatures above the melting point of the metal. The globules of the metal are kept from fusing together by the inert oxide, with which they are mixed, and this enables the calorizing to be done at temperatures at which the metals otherwise would be melted. That is quite an advance in the principle and practice of coating metals by vaporization.

L. D. Vorce: Have experiments been performed on these calorized metals to indicate whether they have chemical properties similar, with respect to various reagents, to the normal metals alone?

W. E. Ruder: In regard to the question of painting large parts with calorizing mixtures, that can be done by mixing up a

paint of thin shellac, or something of that nature. We have tried several schemes for this, but the chief difficulty with that process is that altho it protects all right, it gives too thin a coating. As I have explained in the paper, the continued heating of the calorized article causes the aluminum to diffuse inward, naturally, from the alloy rich in aluminum toward the pure iron, and this gradually cuts down the concentration of the aluminum in the outside area. Very soon, then, if this outside coating is broken, as by rough handling, oxidation of this depleted alloy will begin. That is the chief advantage of putting on a heavy coating first.

In replying to Dr. Richards' inquiry of this morning, I promised to say something about thermocouples. We have tried to calorize them and have met with considerable success. When the question was first put up to me, I said, "No, it can not be done," because we would have a continual change of electromotive force, due to the fact that the aluminum was diffusing inward all the time. Experimental work, however, proved that this fact did not cause any serious trouble, any change of thermoelectromotive force was very slight, and although the experimental work is not yet finished we have found that the base metal couples which have been calorized in several cases gave a life (at 900 degrees) three or four times the life of the uncalorized couple. The calorized couples can be usually run at 1,000 degrees, while the limit of the uncalorized couples is 900° C.

Calorized copper for bus bars for electric furnaces certainly ought to be a great saving. Copper calorizes very easily at about 600° C., even lower. We usually run at about 600° because we get a little more rapid deposit. The method has been very successful in the case of all the copper parts we have calorized, and also on soldering irons, which was one of the subjects asked about.

Mr. Mott's explanation of why aluminum should be so much better than magnetite is certainly true, but I do not think it has the weight that the other reason has, namely, that in calorized parts we find that the thin coating does not give us nearly the service a heavy coating does, for the reason that the thin coating in any kind of severe service will crack, so that the advantage of putting on a heavy coating is that there is always a supply of aluminum to oxidize in case the outer coating breaks.

There are several processes for coating iron or metals, even non-metals, with aluminum, which serve to a certain extent the same purposes as calorizing does, but they are limited in their application. There is a process for dipping iron or metals into tin and then dipping them into the molten aluminum, which gives a very good coating, but it is only a surface coating, and once it is broken down the metal begins to burn immediately.

There is also another process which really amounts to aluminum painting, and is only a very adhesive paint. This also protects the surface and stands a slight amount of heat, but the least jarring or scraping of the surface will start oxidation.

As to the chemical properties of this product we know very little of them, except that it has high resistance to most of the acids, and it has more resistance than the metal itself. That is shown very easily on these etched samples which you have examined. If you leave one of these samples in nitric acid for a considerable length of time, the iron will etch away, leaving most of the coating, but the coating also disappears gradually.

The point should also be brought up that calorized iron forms no protection against ordinary atmospheric corrosion, it rusts through. Calorized copper, on the other hand, will stand atmospheric corrosion very well, better than aluminum bronze, because we have a much richer aluminum alloy on the surface.

Jos. W. Richards: May I ask what the increase of weight is; have you determined it in any case?

W. E. Ruder: It is pretty hard to say. It would be different in every case. We calorized different parts. If you take a very thin part the calorizing goes right through, and of course, taking the heavier tubes we have only a small surface change. An average value of increase in weight is about six percent. There is a change of about 1 mil or 2 mils (0.025 to 0.05 mm.) in the diameter of the piece.

A paper presented at the Twenty-seventh General Meeting of the American Electrochemical Society, at Atlantic City, N. J., April 22, 1915, President F. A. Lidbury in the Chair.

"FIBROX"

By E. Weintraub.

(I) Introduction.

Fibrox is the name given by the author to a fibrous material of the composition of silicon oxycarbide. The name is to suggest the remarkable structure of the material.

Amorphous silicon oxycarbides have been prepared before and even fibrous materials of that composition in very small quantities and in a more or less accidental manner.

The first to have prepared compounds containing silicon, carbon and oxygen were Schuetzenberger and Colson. They found in the year 1881[1] that crystallized silicon heated to a white heat in an atmosphere of carbonic acid absorbed that gas and was converted into a greenish white mass, which, after purification by means of potassium hydroxide and hydrofluoric acid, left a greenish powder which corresponded approximately to the formula SiCO. The re-action according to them is

$$Si_3 + 2CO_2 = SiO_2 + 2SiCO.$$

The same substance was formed more slowly at a higher temperature by the direct combination of silicon and carbon monoxide. In the year 1882[2] Colson prepared by other methods, which are of no further interest in this connection, other silicon oxycarbides, and found in particular that by passing a *stream* of carbon dioxide over silicon at high temperature carbon monoxide is evolved and a silicon oxycarbide to which he attributed the formula $Si_4C_4O_2$ is formed.

These silicon oxycarbides of variable composition were all amorphous powders, unattackable by boiling caustic solutions

[1] C. R. Vol. 92, p. 1508.
[2] C. R. Vol. 94, p. 1710.

and hydrofluoric acid not readily oxidized at high temperatures by oxygen, but decomposable by a mixture of chromate of lead and litharge.

Schuetzenberger and Colson succeeded also in preparing in minute quantities a fibrous material, and perhaps it will be of interest to quote their words:[3] "One to two grams of silica is introduced into a crucible of gas-retort carbon and covered by a disc of gas-retort carbon furrowed on its upper surface. In these furrows are placed several decigrams of silicon crystals, and the whole is covered with a well fitting lid. The whole is enveloped in titaniferous brasque and heated an hour and a half to reddish whiteness. The silicon is in large part converted into a greenish white oxycarbide, and very curiously a cylindrical column of greenish white oxycarbide, very light and porous, spread out above and below, runs from the center of the furrowed disc to the center of the lower side of the lid."

Mülhauser[4], in making carborundum from coke, sand and salt, found between the layer of amorphous carborundum and the mixture of unattacked material a fibrous material. He describes it as grayish-green in appearance, the fibres being as long as two centimeters. The amount of substance he had was not sufficient for a carbon determination, and from the determination of silicon and aluminum he attributed to the substance the formula $AlSi_2C_7$.

In 1897, C. Kohn[5] described an accidental product of the carborundum furnace observed at the Carborundum Company's plant at Niagara Falls:

"One other product of the furnace is worthy of note. Tiny, feathery tufts are often found sticking to the carborundum crystals and occasionally the same product is found in larger quantity in the inner parts of the furnace in the form of pale greenish-yellow masses excessively light and extraordinarily like a fungus in appearance. On one occasion a piece quite 18 in. long,

[3] "Si dans un creuset en charbon de cornues on introduit de la silice (1 à 2 gr.) que l'on recouvre d'un disque en charbon de cornues creusé en coupelle sur sa face superieure en placant quelques décigrammes de cristaux de silicium dans cette coupelle; si enfin apres avoir fermé le creuset avec son couvercle tourné on enveloppe le recipient de brasque titanifere et si on chauffe une heure et demie au rouge blanc, on constate que le Silicum est en grande partic converti en oxycarbure blanc verdatre et fait tres curieux, une colonne cylindrique d'oxycarbure blanc verdatre tres leger et poreux, épanouie en haut et en bas reunit le centre de la coupelle au centre de la paroi inferieure du couvercle."

[4] Z. f. anorg. Chemie, 1894, p. 119.

[5] J. of the Soc. of Chem. Ind., 1897, p. 866.

about 4 in. broad and 2 in. thick was obtained. At first this was regarded as volatilized silica but it is really carbide of silicon in an extremely fine state of division."

It is impossible from this distance to tell what the material described by Kohn was, but I am inclined to believe that this material and that found by Mülhauser were similar, and were a fibrous form of silicon oxycarbide.

Further observations on silicon oxycarbide were made in the Carborundum Company's plant, and in 1903 patents were issued to Acheson[6] on amorphous silicon oxycarbide, called by him Siloxicon. By heating carbon and silica in appropriate proportions in a furnace of the carborundum furnace type he produced compounds of a variable composition, such as Si_2C_2O and Si_7C_7O. The products are described as amorphous powders, very refractory, indifferent to all acids except hydrofluoric, resisting the action of hot alkaline solutions and capable of being molded into form and fired to yield a coherent mass.

In June, 1912, a patent was issued[7] to Tone on the manufacture of a fibrous silicon oxycarbide in the carborundum furnace under such conditions that a condensation product containing silicon, oxygen and carbon was formed. The material is described as containing on an average 49.95 percent silicon, 43.6 percent oxygen, 6.45 percent carbon, as having a real density of about 2.3 and an apparent density of 0.15, and its possible value as a heat insulating material is recognized. This material of Tone is distinguished from Fibrox by its high apparent density (about twenty to fifty times that of Fibrox), its high real density, and a lower carbon content. It is doubtful whether Tone ever succeeded in getting his material in quantities or in a regular way.

From my own experience I conclude that Fibrox is the result of a very slow growth, for which the conditions of the carborundum furnace are very unfavorable.

All these previous attempts beginning with the work of Colson down to the work of Tone were unknown to me at the moment when I started the work on Fibrox.

[6] U. S. Patent, No. 722793.
[7] U. S. Patent, No. 1,028,303.

This work has originated from some accidental observations made in the Lynn factory. In melting silicon for the manufacture of silicon resistance rods, the formation of a fuzzy material on the top of the silicon was noticed. My attention was attracted to this, and recognizing the possible value of this material as a heat insulator, I decided to start an investigation to find out the conditions of formation of the material.

(II) Preparation of Fibrox.[8]

The different steps by which the factors essential to the production of Fibrox were discovered would possibly make interesting reading, but for the purpose at hand it will be sufficient to describe the final process adopted.

A muffle (or pot) of a material capable of withstanding a temperature of 1,400°-1,500° C, having its bottom covered with a layer of silicon pieces, is heated in a gas furnace to the temperature of incipient melting of silicon. A muffle of Dixon graphite clay-lined has proved to be suitable. The ends of the muffle protruding outside the furnace are luted on to the muffle in a gas-tight manner. *It is essential that a catalytic agent be used.* One such agent is calcium fluoride.

After a run of a few hours the muffle is found filled completely with Fibrox, which is removed and the operation repeated. It is only necessary from time to time to break up the slag which forms on the surface of the silicon and to add some fresh material.

It is obvious from the process described that Fibrox is a product of slow and quiet growth, and from its composition it must be formed when silicon vapors and carbon dioxide or carbon monoxide react. The silicon vapors come from the silicon. The carbon dioxide comes from the combustion gases of the furnace. One has, therefore, to picture to himself the oxide of carbon slowly diffusing through the pores of the vessel and reacting with the silicon vapors. *This slow interpenetration of the reacting gases is an important feature of the process and is essential if the finest structure is to be developed.*

The fluorspar or other catalyzer used has most probably the

[8] Most of the experimental work was carried on by F. Kroner.

function of keeping the slag (silica?) in a sufficiently soft condition to allow the silicon to "seep" through it and expose a clean surface from which the silicon vapors can freely escape.

At the temperature of the incipient melting of silicon, which is used in this method of manufacture, carbon monoxide does not react appreciably. This was proved by heating the crucible in a furnace, the atmosphere of which was rich in carbon monoxide but poor in the dioxide. In one case the muffle was imbedded in charcoal. In another, the muffle was heated in an electric resistance furnace, the resistor of which was either carbon or carborundum. In neither case was the formation of Fibrox observed except in very minute quantities.

The experiment was then varied by letting carbon dioxide penetrate through the pores of the cover of the crucible either by admitting carbon dioxide into a chamber surrounding this cover or by placing a decomposable carbonate into the chamber. The formation of Fibrox was then proceeding in a normal way.

At *higher temperatures* carbon monoxide is capable of reacting with silicon vapors, producing a variety of Fibrox. This was shown by using a special type of electric furnace in which silicon was made to boil by passing current through it and carbon monoxide admitted. The product obtained, while similar to Fibrox, does not have as fine a structure as the gas-furnace product, is much heavier and is a poorer heat insulator.

(III) Properties of Fibrox.

Structure: The most remarkable thing about Fibrox is its physical structure. In order to appreciate the exceptional properties of the material, one must see it.

Fibrox is a soft, resilient, fibrous material; after gentle compression it returns to its original shape; it can be cut into plates, sheets and rings which are self-supporting.

The material is an agglomeration of exceedingly fine fibres. The diameter of the fibres is in average *about 0.6 micron, or about the wave length of yellow light.* Some fibres are undoubtedly smaller and probably approach 0.3 micron. The attached photomicrograph, which was kindly taken for me by Mr. Ellis of the Standardizing Laboratory of the General Electric Co. (linear magnification of 200) represents a human hair (to the

left), a very thin tungsten filament about 0.75 thousandth of an inch diameter (to the right) and a number of Fibrox fibres. The diameter of fibre is about 1/20 of that of a very fine cotton fibre. Under the microscope the fibres appear to be amorphous, transparent and some of them carry little round beads strung along the fibre. These beads are apparently fused silica.

Density: The apparent density of the material, while varying with the circumstances, is usually between 0.0025 and 0.0030. In other words, it weights only about 2½ to 3 grams per liter. The real density of the material varies with its composition.

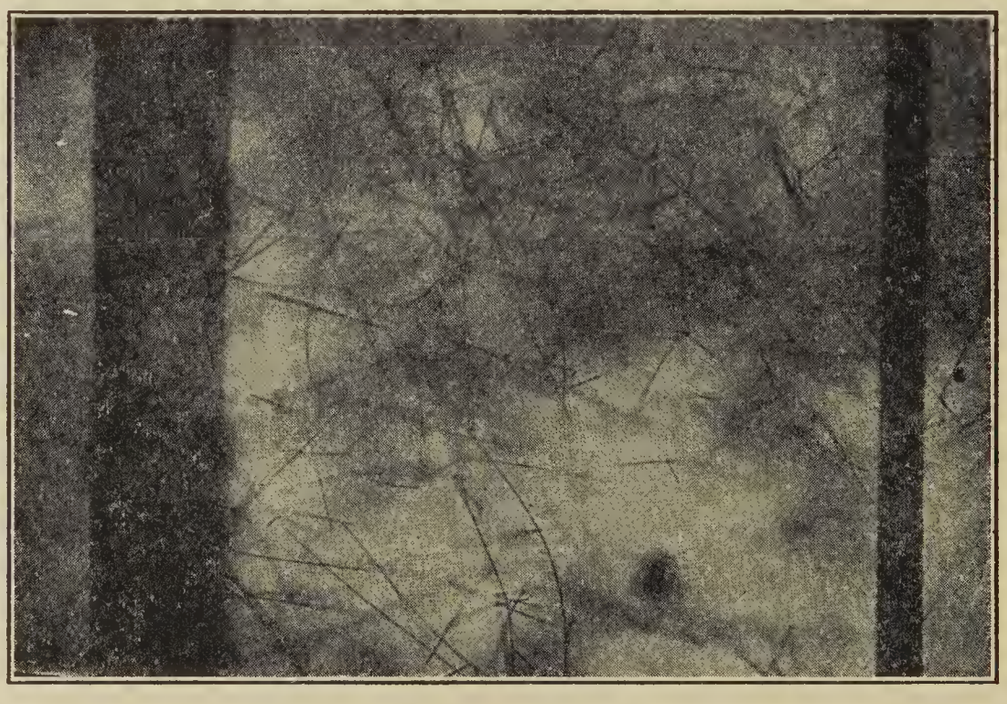

Fig. 1.

When the composition corresponds nearly to the theoretical silicon oxycarbide SiCO (about 21 percent of carbon), the real density is 1.84.[9] As the carbon content diminishes the real density increases up to about 2.2, or nearly that of silica. From the real and apparent density, the actual volume occupied by air is figured out to be over 99.5 percent and in the best cases equal to 99.9 percent and that of the solid material is only from 0.5 to 0.1 percent.

Heat Resistivity: The remarkable physical structure of Fibrox would make one expect it to be an exceptionally good heat insulating material. Measurements for which I am indebted to Mr.

[9] Determined by H. Rush, of this laboratory.

Randolph of the Heating Device Laboratory of the General Electric Co. have shown that Fibrox is the best heat insulating substance known.

For the temperature interval of 100° to 15° a long-fibre dark-green sample of Fibrox compressed to a density of 0.767 lb. per cubic foot or 12.3 grams per liter has a resistivity in degrees per watt, per inch cube, R′ = 1675, or per cm. cube R = 4200.

A comparison with other materials will be instructive. For wool at a somewhat higher density of 0.955 and the same temperature interval R′ (in. cube) = 802 (R/cm. cube = 2000) and at a density of 3.4, R′ = 1100 (R/cm. cube = 2700). Wool has to be compressed to a density of 12 pounds per cubic foot or more than 15 times that of Fibrox to get the same value of heat resistivity.

Eiderdown reaches a value equal to that of Fibrox at a density of 5, or more than 6.5 times the density of Fibrox.

Among the inorganic heat insulators, Monox has at a density of 6.18, R′ = 1000 (R = 2500) and "Elephant Ear"[10] at a density of 8.4, R′ = 1100 (R = 2700).

It will be seen that by its value of heat resistivity Fibrox stands in a class all by itself.

The heat insulating value of Fibrox is smaller at higher temperatures. The specimen referred to above (density 0.767) gave the following values, the lower temperature being always 15° C.

T	R′ in. cube	R cm. cube
100 degrees	1,675	4,190
200 "	1,320	3,300
300 "	1,050	2,625
500 "	878	2,195

But even so, Fibrox is also superior at high temperatures to the other known insulators which can at all be used at those temperatures. To compensate for the drop in the heat insulating value of Fibrox at higher temperatures, it would be necessary to use it at a somewhat higher density, a density which is, however, low as compared to that of other materials.

[10] U. S. Patents, 1072413, 1072414.

The effect of the density on the heat resistivity of Fibrox at temperatures of 200° and 500° is shown by the following table:

Density			Thermal Ohms	
lb. per sq. ft.	g. per litre	Temp.	R' in. cube	R cm. cube
0.231		200	950	2375
0.231	3.7	500	520	1300
0.412		200	1200	3000
0.412	6.6	500	605	1510
0.767		200	1320	3300
0.767	12.3	500	878	2195
1.27		200	1460	3650
1.27	20.4	500	987	2470
1.98		200	1590	3975
1.98	31.7	500	1000	2500

Taking the last value, we see that at the temperature of 500° C. and a density of about two pounds per cubic foot, Fibrox has a resistivity equal to that of Silox, Monox or Elephant Ear at a density averaging about 6 or 7 pounds per cubic foot.

In many heating devices the negative temperature co-efficient of heat resistivity is very desirable but in cases where very high values of heat resistivity at high temperatures are desired, I have suggested the following arrangement. It is probable that the negative temperature co-efficient of heat resistivity of Fibrox is due to the transparency of Fibrox for long heat waves which, being much larger than the diameter of the Fibrox fibres, pass around these through the air which is the main constituent of Fibrox agglomerate. To overcome this it would, therefore, be only necessary to break up the layers of Fibrox by means of absorbing or reflecting walls which would transform the heat waves into molecular heat of lower temperature.

Besides the high value of heat resistivity, all the other properties of Fibrox are such as to make it the ideal heat insulating material. It is perfectly permanent in air and is not hygroscopic.

It is self-supporting, and will not settle down even under the most severe conditions of transportation, etc.

It stands a higher temperature than other insulating materials, such as Monox or Elephant Ear. At temperatures above 1,000°, and up to 1,400°, Fibrox oxidizes in air but very slowly, so that only the layers nearest to the heating units gradually change into silica, a change which does little harm.

The heat capacity of Fibrox is very small, mostly on account of the very small mass of solid material. It is so small that very striking experiments can be made. For instance, a large piece of the material heated up in a Bunsen flame to incandescence can be grasped by the hand immediately after it is pulled out of the flame without any burning effect.

Electrical Conductivity: This is a most puzzling and almost paradoxical property of Fibrox. Fibrox, the best heat insulator, is a relatively good electrical conductor with a conductivity comparable to that of electrolytic solutions.

In making conductivity measurements it is important to secure good contacts and to avoid any sparking at the contacts. If the experiments are carried out in air, the local high temperature due to sparking at the contacts causes oxidation of the contact layer of Fibrox, and the silica film formed acts as an insulator. If due care is exercised and especially if alternating current is used, good measurements can be secured in air. In hydrogen and in carbonic acid or carbon monoxide good results are obtained a little more readily, although sparking must be avoided as much as possible to prevent disintegration, decomposition and pitting at the contact surface.

The following table gives a set of measurements carried out in an atmosphere of hydrogen. The piece had a cross-section 2.7 x 1.8 cm. and a thickness between the copper disc electrodes of 2 cm. No compression was used. The apparent density of the material was 3 grams per liter. The table below gives (1) the voltage across the piece of Fibrox, (2) the amperes and (3) the resistance.[11]

Volts	Amps.	R
8.7	0.05	174
12.1	0.10	121
16.7	0.18	93
21.0	0.35	61
28.6	0.71	40
36.0	1.14	31.5
40.5	1.66	24.5
42.0	1.92	22.0
43	2.32	18.5
46	3.20	14.3

[11] Measurement by A. E. Hibschman, of this laboratory.

The specific resistance per cm. cube at the low current is about 360 ohms. When the piece carried 3.2 amperes, and had a temperature of about 800° C., the resistivity dropped to 30 ohms.

From this the specific resistance of the Fibrox *material itself* at or near ordinary temperature would be less than 1 ohm per cm. cube, and at 800° C., less than 0.1 ohm.

Compression of the Fibrox without destroying its structure increases the conductivity, but if the Fibrox structure is destroyed the conductivity disappears. In other words, each transparent fibre of Fibrox is a good electrical conductor.

The conductivity of Fibrox varies with its composition and appears to increase with the carbon content.

West Lynn, Mass.

DISCUSSION.

F. J. Tone: The material "Fibrox" described by Dr. Weintraub and the material described by me in the patent he refers to are one and the same product. Any differences that exist are differences in degree and not in kind. The identity of the two products is not a proper question for me to discuss here, and I only wish to say in passing that Dr. Weintraub's gratuitous remark that "it is doubtful whether Tone ever succeeded in getting his material in quantities or in a regular way" does not, it seems to me, add anything to the technical or scientific value of the paper.

An interesting point in regard to these fibrous silicon oxycarbides is the absence of any fixed chemical composition. In this respect they resemble the silicon oxycarbides of the siloxicon class. The carbon content varies from 6 percent to 21 percent and with this variation there is a regular variation in the silicon and oxygen content and also in the physical properties of the product. As the carbon increases the absolute density and apparent density decrease in regular gradient. There is also a regular decrease in the size of the fibre. The size of "fibrox" fibres with a carbon content of 21 percent is stated to average 0.6 micron. The size of the fibres of the material I have described with the

lower carbon content averages one micron. The solubility of the product in hydrofluoric acid also varies inversely with the carbon content, ranging from 30 to 70 percent. I therefore can not agree with Dr. Weintraub in his contention that a fixed line of demarcation exists between these various fibrous products.

WALTER ARTHUR: Dr. Weintraub has overlooked, or perhaps is not aware of, some of the work done at Schenectady on this material. Mr. J. H. T. Dempster of Schenectady prepared a small quantity of this fibrous material by passing illuminating gas over molten silicon. This experiment was made sometime before the investigations were started at Lynn.

I attempted to prepare this material in the electric furnace and succeeded in getting it in small quantities; but discovered after a number of trials that the chief difficulty arose from the fact that it is only possible to prepare it through a narrow range of temperature. As Dr. Weintraub has indicated, the temperature must be above that of the molten silicon. But if the temperature is carried higher, how much higher I can not say, this fibrous material decomposes and is replaced by carborundum crystals.

In some of my attempts to prepare this material in a coke resistance furnace I found in the chamber left for its collection a quantity of the black shiny carborundum crystals, with small quantities of the greenish fibrous material around the outer edges of the chamber and in the cooler parts. In many instances these fibers were joined to the crystals of carborundum. Occasionally a small piece of this fibrous material would have a number of crystals of carborundum on one side. What had probably happened was that the contents of the chamber, after being filled with this fibrous siloxicon, had decomposed, allowing carborundum to be formed. This might lead us to believe that silicon is the first step in the formation of carborundum. It will be recalled that the granular, greenish siloxicon is always found in carborundum furnaces in the cooler zones just outside of the carborundum.

There are some very interesting properties of fibrox which Dr. Weintraub has not discussed. If a piece of this material be made a part of an electric circuit in such a way as to produce an arc at one side, a portion of it will be decomposed with explo-

sive suddenness yielding a whitish smoke and leaving small round holes. This phenomenon is what was referred to as pitting. The quantity of the material decomposed depends upon the voltage, which controls the length of the arc and the heat generated. That the whole of the material is not decomposed is probably due to the fact that it is a poor conductor of heat.

Another characteristic of this substance as interesting and striking as its conductivity is its tendency towards polarization. If a piece of it be lightly clamped at either end so as to make good electrical connections and a small current passed through it and slowly raised, one end will be seen to become red while the other end remains cool. If the current is reversed the opposite end is heated; if it is again reversed the heating is reversed.

H. K. Hitchcock: This material brings back very vividly to me a series of experiments which I made a good many years ago, and I am wondering if this material may not account for the phenomena I observed at that time. I had a recrystallized carborundum crucible imbedded in a granular carbon resistor furnace, in which I used to vaporize sand or SiO_2. In the crucible itself, above the boiling silica there would be no indication of vapor, but there would be a perfectly clear space for a considerable distance above the top of the crucible. Above this, however, there would be very tangible, fine cobwebby clouds that would float off, and had the characteristic color of this material. I always accounted for this phenomenon as being the result of the vaporization of the silica and its condensation as it cooled off higher up, but I now wonder if there was any relation between this cloud effect and this material.

W. S. Franklin: I was very much interested in the apparent polarization of this material. It seems to me that it is due to the development of a temperature high enough at both electrodes to start gas ionization, and then, when the ionization of the gas or the air begins, the development of a very much greater amount of energy at one electrode than the other, because of the different mobility of the positive and negative ions. I think that the polarization is not a property of the material, but is due to the

enclosed air and is a phenomenon of gas conduction rather than a phenomenon of conduction by this solid material.

E. F. NORTHRUP: Referring to the question of asymmetry in the conduction, I recently did some experimenting which may throw some light on the fact and show that it is not peculiar to fibrox or any other material. I will give you a few definite data on this. I took a cylinder of graphite and located axially in it a tungsten wire. Means were provided for measuring the passage of current from the wire to the cylinder when the temperature was raised to 1,510° C. and when nothing was in the cylinder other than CO gas plus perhaps a little nitrogen. With the center made plus the current curve ascends in one way, and with the center made minus the curve ascends in another way. You will note that the current is about 65 milliamperes when the voltage is 108 volts and at this voltage the current is the same whether the center is made positive or negative, but that at all lower voltages the current is much less if the center is made minus than it is if the center is made plus, and that the reverse is true when the voltage exceeds 108 volts. (These curves are shown and the experiments described in an article by me in the Journal of the Franklin Institute, March, 1915.)

The asymmetry was found to be some function of the diameter of the center electrode and probably also of the temperature. With a passage of 65 milliamperes at 110 volts there is an output of over 7 watts and a consequent rise of temperature at the surface of a fine wire used as a center electrode. Such are the facts when there is nothing but gases in the furnace. If this space around the center electrode were to be filled with any refractory, such as aluminum oxide or fibrox, I think it is almost certain that there would be asymmetry in the conduction which would grow less as the diameter of the center electrode is increased. When the diameter of the inner electrode becomes nearly that of the inside diameter of the outer cylinder there probably would be very little or no asymmetry. So much for that point.

There are three classes of papers one might discuss. First, there are those which one wishes to analyse and point out errors. Second, those to which one wishes to contribute new matter, and

third, those in which I class this one, where the only reasonable thing to do in the discussion is to ask questions. I have made a list of questions here but if I ask them and obtained answers we would not have much time for other papers. I will only ask one or two. Have the properties of this material, after it has been very highly compressed under hydraulic pressure, been studied? May I ask also if fibrox has good filtering properties?

The thought came to me as I listened to this paper that nature spent several million years in evolving a heat insulating covering for the whale in the form of blubber, and for the eider-down duck in the form of down, and that it is rather interesting to note the General Electric Company can evolve in a few months a better heat insulator than nature can evolve in working several million years.

President Lidbury: I would like to ask Mr. Arthur whether in connection with the apparent polarization he took the trouble to see on breaking the circuit if there was a back electromotive force present.

Walter Arthur: I did not. The probable explanation of this thing is that it is due to the flow of current from sharp points to flat surfaces, perhaps nothing more.

L. H. Baekeland: Very little has been mentioned about the chemical properties of this substance, I am very curious to know how sulphuric acid, caustic soda, or caustic potash acts on it.

H. S. Taylor: There is one point which I think ought to be raised in connection with this paper. It is a point which from the very fact that it is placed in italics, seems to be of considerable importance. What I refer to is the statement on page 270, as follows: "It is essential that a catalytic agent be used." Dr. Weintraub in the course of his address told us that the function of the fluorspar or calcium fluoride, or whatever it is that is added, seems to be to remove the silica which is formed in the course of the reaction, and further on he says: "It is only necessary from time to time to break up the slag which forms on the surface of the silicon and to add some fresh fluorspar or other catalyzer." I should like to raise the point as to whether under these conditions the fluorspar is legitimately called a cata-

lytic agent, as I was under the impression that a catalytic agent was such as could be used over and over again and did not disappear in the course of reaction.

CARL HERING: I notice that the resistance of the sample piece decreases very fast as the current increases, which I understand means that the piece was being heated by the current. This would seem to indicate that the resistivity may decrease so fast with an increase of temperature produced by the current, that there may be danger of passing the unstable point at which the temperature goes on increasing so rapidly due to the increase of current that ultimately the piece would be destroyed. It would be interesting to know what the results were, if the author has tried this.

L. E. SAUNDERS: On page 269 Dr. Weintraub states that from his experience fibrox is the result of very slow growth for which the conditions of the carborundum furnace are very unfavorable. On page 270 he states that after a run of a few hours the muffle is found filled completely with fibrox, which is removed and the operation repeated. If a carborundum furnace were run with the intention of making fibrox, I think a very much more economical production could be secured than in the few hours he described with the muffle furnace. As a general rule, the carborundum furnace is not run to make fibrox, but carborundum.

WALTER ARTHUR: In reply to what Mr. Saunders said, that would be very true, provided we can control the temperature, but if the temperature goes up to some value like 2,200° or 2,300° C., the silicon oxycarbide of this fibrous material is decomposed. I tried it many times, and got small quantities of it, but as the temperature got higher the carborundum crystals would take its place. It is easy enough to get this material, but to prevent it from being destroyed is another proposition entirely.

L. E. SAUNDERS: I think it is very much easier to control temperatures in a furnace of commercial size than it is in a furnace of such a size as most experimental laboratories can run.

WALTER ARTHUR: I can not agree with that.

L. E. SAUNDERS: Did you have any experience with commercial furnaces?

WALTER ARTHUR: Yes, two months working on this very proposition and with commercial furnaces, too.

W. R. MOTT: Dr. Weintraub has spoken of the unusual translucency of fibrox in relation to its electrical conductivity. Like properties are shown by carborundum which is a conductor at ordinary temperatures and in small crystals is translucent if fairly pure.

The chemical reaction between calcium fluoride and silica takes place at a fairly low temperature (somewhat at even 600° C.) giving gaseous silicon tetrafluoride, which would break up the surface crust. The equation of the reaction can be as follows:

$$2\ CaF_2 + 3\ SiO_2 = SiF_4 + 2\ CaSiO_3$$

Other reactions are possible with free silicon, silicon monoxide and carbon and I am hoping Dr. Weintraub will discuss these mysterious reactions.

JOS. W. RICHARDS: Dr. Hering has called attention to the electrical measurements of the resistivity. I am convinced that the resistances given do not represent the correct resistivity of the material, and for the following reason. If you calculate the amount of energy which is generated by passing a current of 3 amperes dropping 46 volts, through the small piece of fibrox used, weighing only 30 milligrams, it would raise its temperature 6,000° C. in one second.

FRANCIS C. FRARY: I would ask Mr. Arthur if it was true, as it is apparently assumed, that the decrease of heat showed at the positive side of the circuit in the asymmetrical development of the heat?

WALTER ARTHUR: Yes.

E. WEINTRAUB: Answering the remarks of Messrs. Tone and Saunders, I see no reason to change my ideas on the formation of fibrox in the carborundum furnace. Everyone seems to agree that in the furnace as run at present the yield of fibrox is very small, and that the material is as a rule heavier and coarser.

Mr. Saunders thinks that by changing conditions the yield might be greatly improved. Mr. Arthur, who tried to do this very thing, failed, and he points out the reasons why success in this direction is improbable.

It is true that the growth of fibrox in the gas furnace is slow, as far as weight produced is concerned; the volume relations are much more favorable, however, and the commercial value of the process will be determined by the cost of production *per unit volume.*

Answering Professor Northrup's question, the absorbing and filtering qualities of this material offer peculiarities which I hope to describe later.

Fibrox can be readily compressed into a coherent mass without the addition of any binder other than water; using a pressure of a few hundred pounds to the square inch, crucibles and other vessels were made which can be used at high temperatures very much like silica vessels.

Regarding Mr. Baekeland's inquiry as to the chemical properties of the material, these depend somewhat on the composition, which is very variable, as Mr. Tone has already pointed out. The material of the ideal composition SiCO is not attacked by caustic alkali under ordinary conditions, nor is it affected by sulphuric acid at ordinary temperatures.

One of the speakers objected to the designation of fluorspar as a catalytic agent, since it has to be replaced from time to time. This objection is not justified. We are used to call a catalytic agent any substance which accelerates a reaction without apparently taking part in it. The agent may be removed due to unavoidable physical forces (diffusion, convection, etc.), or the presence of "poisons," without losing its character of a catalytic agent.

With regard to asymmetrical conduction, I am rather inclined to believe that under proper conditions no polarization appears. The trouble is possibly entirely accounted for by bad contact. A bad contact between the electrode and the extremely small ends of the fibers readily develops into an incipient spark resulting in a high local temperature and subsequent polarization. The high temperature decomposes the material at the surface, and

if the experiment is carried out in air, oxidation takes place. In either case a non-conducting film is produced.

Answering Mr. Hering's question, placing a piece of fibrox across a definite voltage without any resistance in series naturally leads to a short circuit; with resistance in series the conditions of stability are those which I have described in my publications on boron.

Professor Richards figures out a temperature of about 6,000 degrees for the piece of fibrox used in my conductivity measurements. Professor Richards must have done some very rapid figuring. In the actual experiment the temperature did not exceed 800° to 900° C. I think that if Professor Richards goes over his calculations, taking into account the enormous radiating surface of the fibres constituting the material, everything will come out all right.

I can't commit myself on the question of price, but I should think that on a large scale of production the material would cost somewhere between twenty and fifty cents per cubic foot.

No one brought up the question of cost of transportation. That may be as serious a problem as any connected with the manufacture itself.

A paper presented at the Twenty-seventh General Meeting of the American Electrochemical Society, at Atlantic City, N. J., April 22, 1915, President F. A. Lidbury in the Chair.

THE THERMAL CONDUCTIVITY OF REFRACTORIES.

By Boyd Dudley, Jr.

The usefulness of correct data in regard to the thermal conductivity of refractories and other materials used in the construction of metallurgical and industrial furnaces is quite generally recognized. Numerous investigations of this property of refractories have been conducted, and in many cases the published data of different investigators are somewhat conflicting. This is particularly true of figures pertaining to materials intended for use at high temperatures, and it is with such materials that the metallurgist is most interested. The difficulties in the way of precise determinations of thermal conductivities at elevated temperatures are numerous, and it is not particularly surprising that there exists a set of data for each method of determination, the figures of which fail to agree closely with those obtained by other methods. However, it should be remembered that the variations in the figures of different observers are doubtless due to variations in the materials tested as well as to differences between, or inaccuracies of, the methods employed. The present paper deals with the methods and results of an investigation designed to develop a practical and reasonably accurate means of determining the thermal conductivity of regular kinds of brick, under conditions approaching those of practice, and without the necessity of preparing special shapes or samples of the materials being tested.

In reviewing the methods that have been used and proposed for determining the conductivity of refractory materials, they fall naturally into three general classes, calorimeter methods, measured heat-input methods, and comparison methods.

The calorimetric measurement of conductivity consists of heating the substance to be tested on one side while the other side is in contact with a water-jacket or other cooling device. The rate

of heat flow is determined by measuring the rise in temperature of the water flowing through the jacket together with the rate of flow. Temperatures are measured at various points in the test piece, and from these data, together with a consideration of the size and shape of the body under test, the conductivity may be calculated. This method was used by Wologdine[1] in an extended research involving the determination of porosity as well as of conductivity of a number of refractories. In these experiments the specially prepared round test piece was inserted into a hole in the top of a small gas furnace. The test piece was heated on the lower side and the calorimeter was applied to the upper side. Temperatures were measured by means of thermocouples at various points within the test piece. From the description of the method it would appear that the precautions taken against heat transfer from the surroundings to the water in the calorimeter were inadequate, and apparently this point was not considered in calculating the conductivity of the test pieces. The calorimeter method was used by C. P. Randolph[2] in determining the conductivities of compressible materials and powders such as lamp-black, magnesia, asbestos, etc. In this case the material being tested was pressed between an electrically heated copper plate and the calorimeter, which was round in shape and constructed in two compartments, one surrounding the other. Both compartments were maintained at the same temperature; the outer compartment thus constituted a guard ring or insulator, which protected the inner compartment from gain of heat through its sides. A modification of the calorimeter method was used by Hutton and Beard[3] in a study of the conductivity of finely powdered fire clays and similar materials. Instead of a water calorimeter they employed a brass disk in contact with the cool side of the material being tested, and estimated the rate of heat flow by heating the disk to the temperature that it attained in the experiments and allowing it to cool in air. By noting the rate of cooling, the rate of heat loss was calculated from this and from the weight and specific heat of the disk.

The measured heat-input method involves the construction of

[1] Electrochem. and Met. Ind., **7**, 383 (1909).

[2] General Electric Review, **16**, Feb. (1913); Trans. American Electrochem. Soc., **21**, 545 (1912); Met. and Chem. Eng., **10**, 287 (1912).

[3] Electrochem. and Met. Ind., **3**, 291 (1905).

a furnace or hollow test piece of the material to be tested, on the inside of which heat is generated at a measured rate by means of an electric current. When thermal equilibrium has been established, temperature measurements are made at various points on the walls of the furnace or test piece. From these data the thermal conductivity of the material may be calculated, taking into account, of course, the size and shape of the furnace. This method was employed by Clement and Egy,[4] who used specially prepared cylinders of fire-clay heated internally by means of a resistance coil of nickel wire. Hering[5] proposed the use of a hollow sphere of the refractory material filled with and surrounded by suitable liquids, or, as a substitute for the sphere, a cylindrical cup with hemispherical ends. The liquid on the inside of the container is to be heated by electricity. FitzGerald[6] compared the conductivities of various refractories by constructing a small cubical furnace of each and heating it internally with a resistance of nichrome wire. The comparison was obtained by determining the maximum temperatures attained by each furnace at various rates of heat generation. Richards[7] compared the conductivities of electrode carbon and electrode graphite by heating a small cubical furnace constructed of each material by means of an electric arc, the comparisons being effected by measuring the energy input and the internal and external temperatures of the furnaces. As a means of comparing the thermal conductivities of refractory materials the measured heat-input method possesses the advantages of simplicity and ease of operation. But the satisfactory calculation of the conductivity from data thus secured is usually a difficult matter, owing to the facts that the more or less complicated and uncertain shape factor[8] of the test piece must be considered and that the conductivity is rarely constant over any great range of temperature.

A comparison method differing from all of the above has been suggested by Northrup,[9] who proposes placing the body, the

[4] Bull. 36, Eng. Experiment Sta., Univ. of Ill., Urbana, Ill.; Met. and Chem. Eng., **8**, 414 (1910).

[5] Trans. Am. Electrochem. Soc., **18**, 213 (1910); Met. and Chem. Eng., **8**, 627 (1910).

[6] Trans. Am. Electrochem. Soc., **21**, 535 (1912); Met. and Chem. Eng., **10**, 286 (1912); Met. and Chem. Eng., **10**, 129 (1912).

[7] Trans. Am. Electrochem. Soc., **24**, 109 (1913); Met. and Chem. Eng., **21**, 575 (1913).

[8] Langmuir, Trans. Am. Electrochem. Soc., **24**, 53 (1913); Met. and Chem. Eng., **11**, 574 (1913).

[9] Met. and Chem. Eng., **11**, 572 (1913); Trans. Am. Electrochem. Soc., **24**, 85 (1913).

conductivity of which is to be measured, in contact with another body, the conductivity of which is known, and then passing heat through the two in series. By measuring the temperatures at the surfaces of the two materials the temperature drop through each may be found and thus a comparison of their conductivities may be obtained. If the conductivity of one is known, that of the other may be calculated. It is of course necessary to know the conductivity of the standard body at various temperatures, and the practicability of the method depends upon the possession of this knowledge.

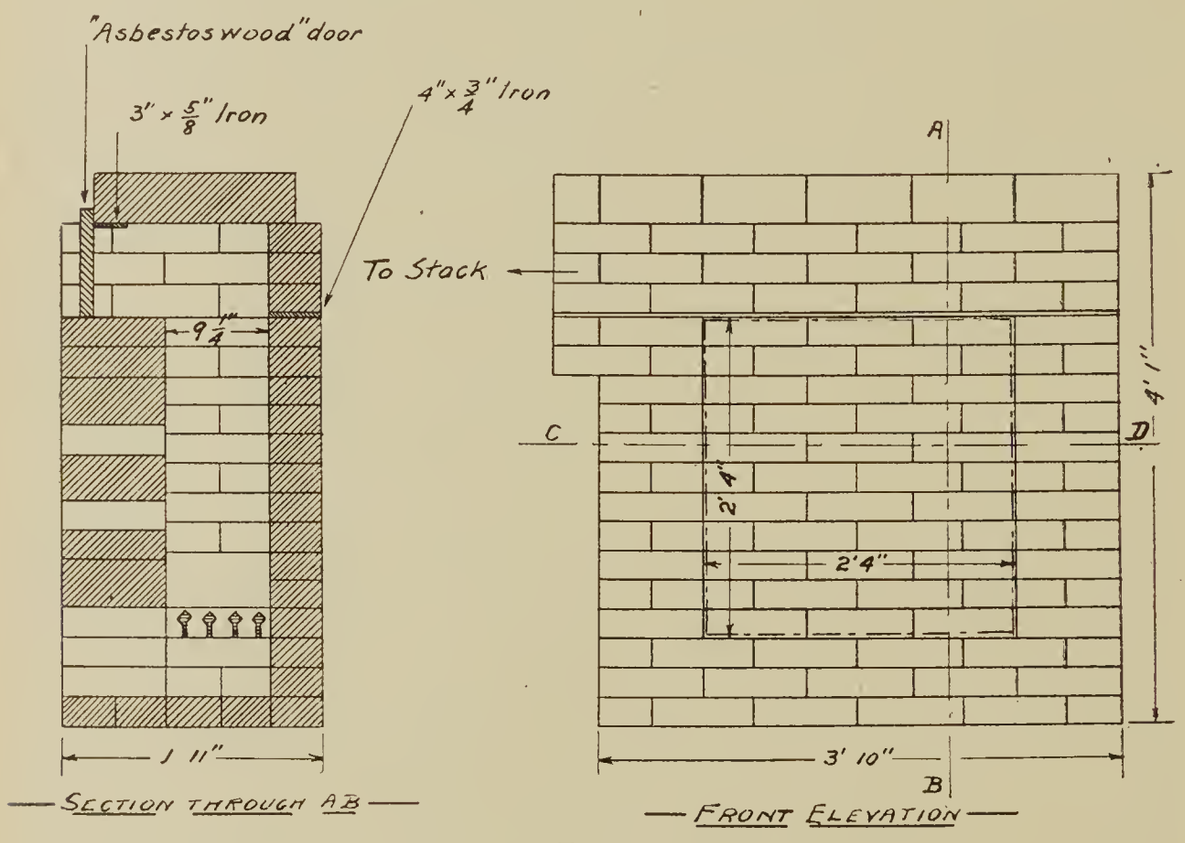

FIG. 1.

The method of determining thermal conductivities employed by the writer consists of heating a wall of the brick being tested with a specially constructed coke-fired furnace, and measuring the rate of heat flow through a certain area of the wall by means of a water jacket applied to the cold side. Temperature measurements are made at various points in the brick, and from the data thus secured the conductivity of the material constituting the wall is calculated. The advantages of the method are these: Special shapes or test pieces of the refractory are not needed, the tests being made on samples of commercial brick. The con-

ductivity is readily calculated from the observed data without recourse to complicated factors involving the shape of the conducting body. Variation of the conductivity with temperature is made apparent by graphic representation of the temperature gradient through the brick.

The construction of the furnace is shown in Fig. 1 and Fig. 2. It consists of three permanent walls, one side and two ends,

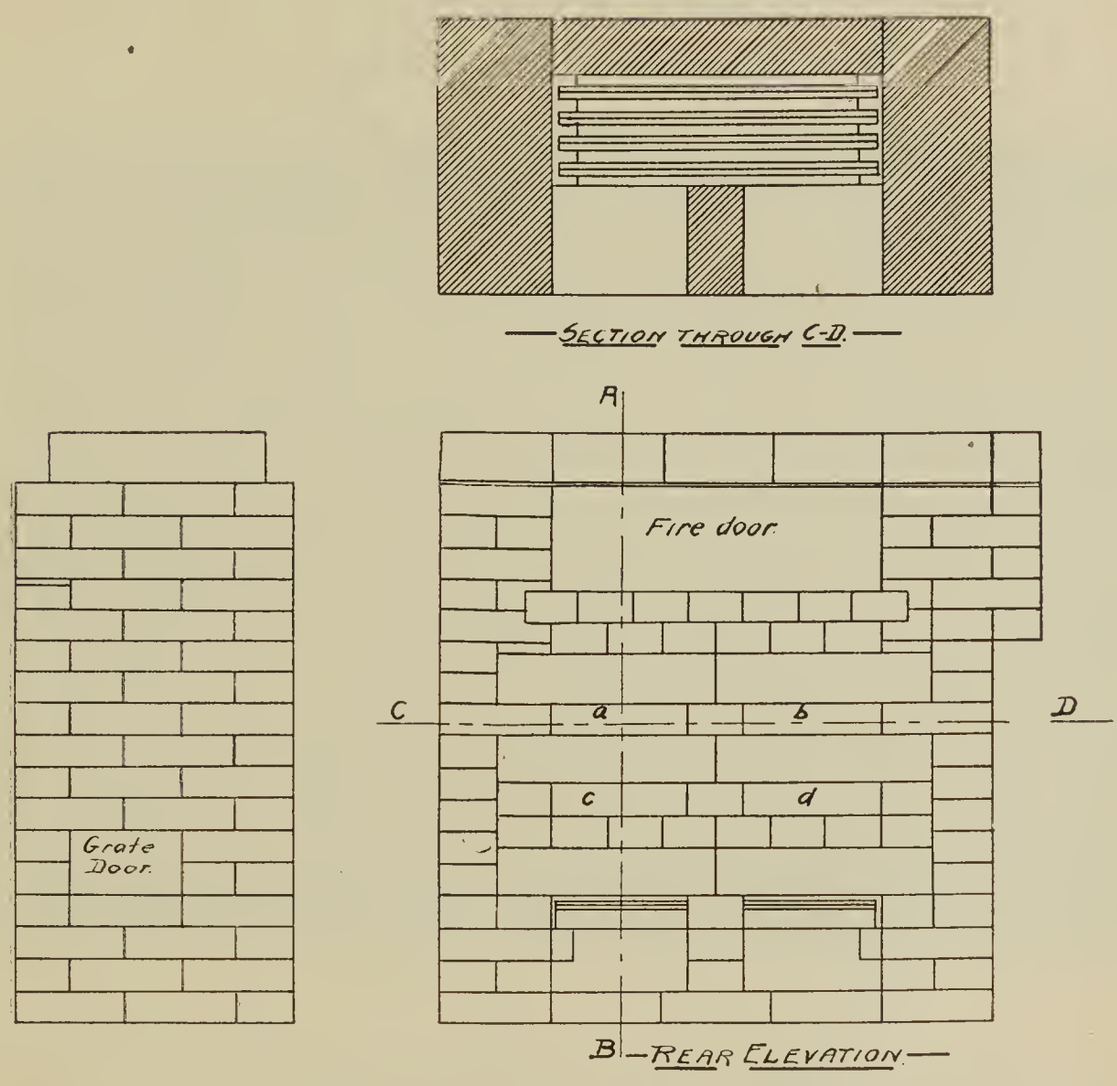

FIG. 2.

provided with a permanent roof and stack connection. These three walls are constructed of fire brick and tile, and are each nine inches thick. The roof of the furnace and the stack connection are supported from the end walls on iron bars placed as shown. The third wall, outlined in Fig. 1 by a dot and dash line, is one brick (4½ inches, 11.3 cm.) thick and is independent of the other parts of the furnace. This is the part of the furnace used for the determinations, the wall being built of the brick

to be tested. The fuel used is sized by-product coke, which is charged through the fire door at the top of the back side of the furnace. The grate consists of four iron bars placed as shown. Air enters under the grate, and additional air is drawn through the openings *a, b, c, d,* (Fig. 2) in the back side of the furnace.

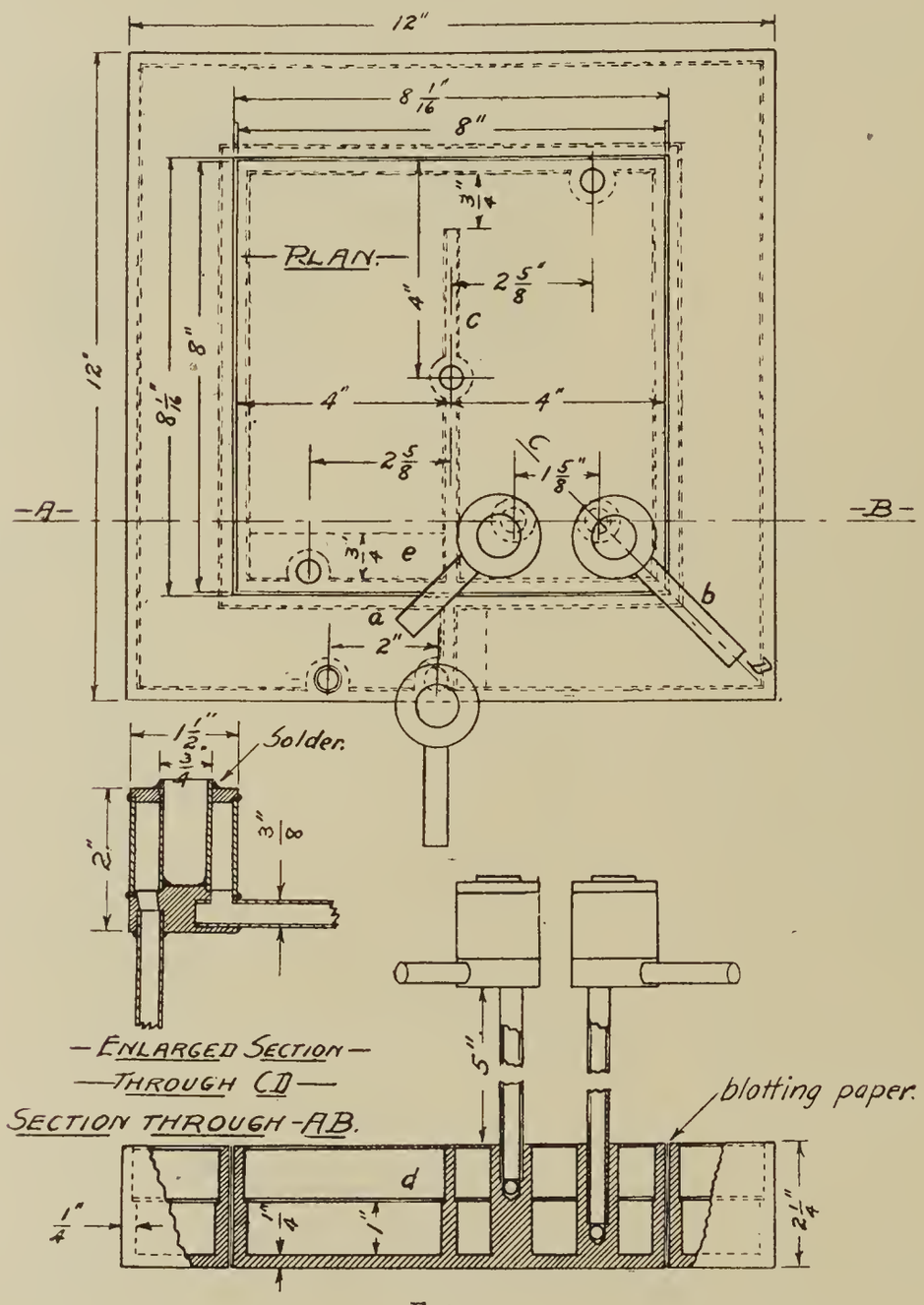

FIG. 3.

These openings may be closed or left open as is necessary; it is found that by regulating the amount of air entering the furnace at the various points it is possible to secure rapid combustion of the coke from the top of the bed of fuel to the grate, a depth of about 26 inches. In this manner a sufficiently large area of

the test wall is heated to a uniform temperature to render permissible the use of a calorimeter one foot square. The test furnace was constructed at the back of a large coal-fired assay furnace, and was connected to it so that the products of combustion entered the latter through its fire door and then passed to the stack. A general view of the furnace with the calorimeter in position is shown in Fig. 4.

As indicated in the preceding paragraph, the front wall of the furnace is constructed of the brick to be tested. Thirty standard

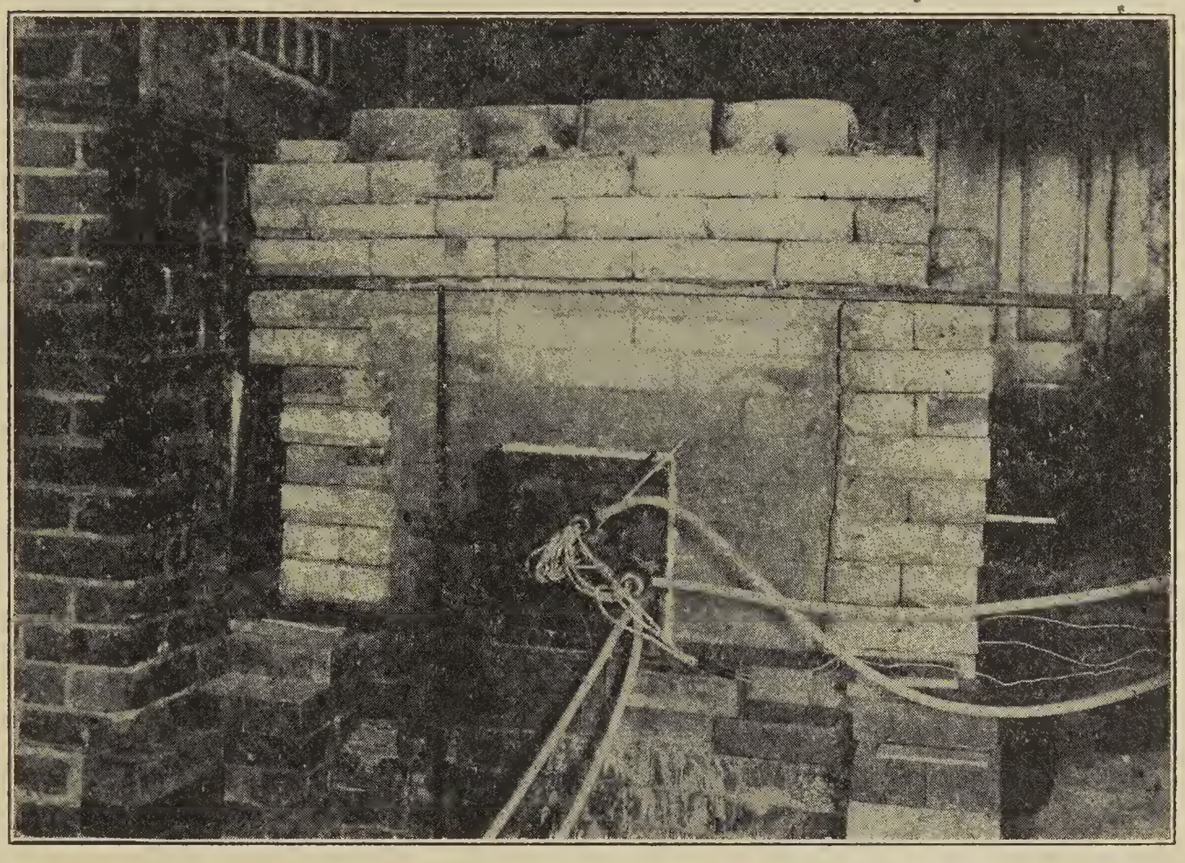

FIG. 4.

nine-inch brick are needed. They are specially selected with reference to regularity of size and shape, perfection of edges and corners, and good workmanship in general. The brick are first laid out on the floor in the exact position that they will occupy on the wall. They are thus arranged in the manner best suited to give a wall of smooth surface and thin joints. Each brick is then numbered and marked so that it may be placed in the wall in the position determined upon. Three of the brick are notched in their under surface in such a manner that when the wall is laid there will be three holes extending into the brick

to a depth of 4¼ inches (10.6 cm.). The position of these notches is such that the holes in the finished wall will coincide with the three holes through the inner compartment of the calorimeter; see Fig. 3. The notches are carefully cut in order to make them of uniform cross-section and exact length. The depth of the notch is about ⅛ inch (0.3 cm.), the width at the top being about the same. The length of the notch is 4¼ inches (10.6 cm.), which makes the hole in the finished wall the same in depth. Since the thickness of the wall is 4½ inches (11.3 cm.), that being the width of the standard brick used, ¼ inch (0.7 cm.) of brick is left at the back of the hole. The brick are laid with great care to secure a wall with smooth face and joints of the least possible thickness; a thin mixture of finely ground fire-clay and water is used in the joints. When the notched brick are laid a piece of copper wire ⅛ inch (0.3 cm.) in diameter is first placed in the notch, then the notched surface of the brick and the ends are covered with the fire-clay and water mixture, after which the brick is pressed and tapped into its place. At the end of about an hour the copper wire is withdrawn from the brick with a rotary motion, which leaves a smooth hole slightly greater than ⅛ inch in diameter and extending 4¼ inches into the wall. The position of the three holes in the finished wall coincides, as was explained above, with the three holes through the inner compartment of the calorimeter; they are spaced one layer of brick (2½ inches, 6.3 cm.) apart in vertical distance and approximately 3½ inches (8.8 cm.) apart in horizontal distance. Thus the temperature of the wall is taken during a test at three points, one being at the center of the inner compartment of the calorimeter, the others being at the upper left-hand corner and the lower right-hand corner of this compartment, respectively. After the test wall is completed the three pyrometer holes are plugged with tightly fitting pieces of wood, all lumps on the face of the wall are carefully dressed down, and the entire surface is painted with a mixture of neat Portland cement and water. In this manner a smooth and practically plane surface is produced, against which the calorimeter may be snugly fitted. The back or fire side of the wall is covered with a thin layer of cement and fire clay, which is well troweled to a smooth surface. The completed wall is thoroughly dried by heating it for several days

with an electric resistance heater consuming about 1.5 kw., which is placed in the bottom of the furnace.

The construction of the calorimeter, with which the rate of heat flow through the wall is measured, is shown in Fig. 3. It consists of two independent compartments, one of which is surrounded by the other. The inner compartment is 8 inches (20.3 cm.) square, and consists of a brass casting finished on the sides and base, to which is soldered a cover of sheet brass. The water connections and interior partitions are so arranged as to provide for thorough circulation of the water within the calorimeter. Water enters through the tube marked *a* (Fig. 3) and passes out through the tube marked *b*. It circulates within the compartment by passing around the end of the interior partition *c*, while on the side of the diaphragm marked *d*; at the point *e* it passes to the opposite side of the diaphragm, and then by passing around the end of the partition *c* it reaches the exit pipe *b*. The outer compartment is 8-1/16 by 8-1/16 inches (20.5 cm.) inside and 12 by 12 inches (30.5 cm.) outside. It consists of a brass casting finished on the base and on the four inner sides, *i. e.*, those sides that face the inner compartment. The arrangement of this compartment for securing thorough circulation of the water is similar to that of the other. The inlet and outlet tubes of the inner compartment and the outlet tube of the outer compartment are each provided with a small double-walled cylindrical water-jacket through which the water has to pass; the construction of these cylinders is shown by the sectional drawing through C-D, Fig. 3. The materials used are sections of brass tubing and brass disks turned as shown. The rise in temperature of the water flowing through the inner compartment and the difference in temperature of the outflows from the two compartments are determined by means of thermocouples carried by rubber stoppers, which are inserted into the open tubes of these cylindrical water-jackets. To provide an outlet for air that is trapped by both compartments of the calorimeter in the spaces above the water outlets, small copper tubes are attached at the top edge of each compartment. When the calorimeter is placed in position against the wall the tubes are allowed to remain open until all of the air is expelled, as indicated by the passage of a continuous stream of water through each; then they are closed by pinching the ends

with a pair of pliers. At intervals of a half hour during a test one or more of the tubes are opened in order to release any air that may have collected. The outer compartment carries four tubes, two on each side of the diaphragm. Only one tube is attached to the inner compartment, the space on the opposite side of the diaphragm being vented by means of a small hole 1/32 inch (0.8 mm.) in diameter drilled through the diaphragm. This hole allows the escape of air from the back side of the

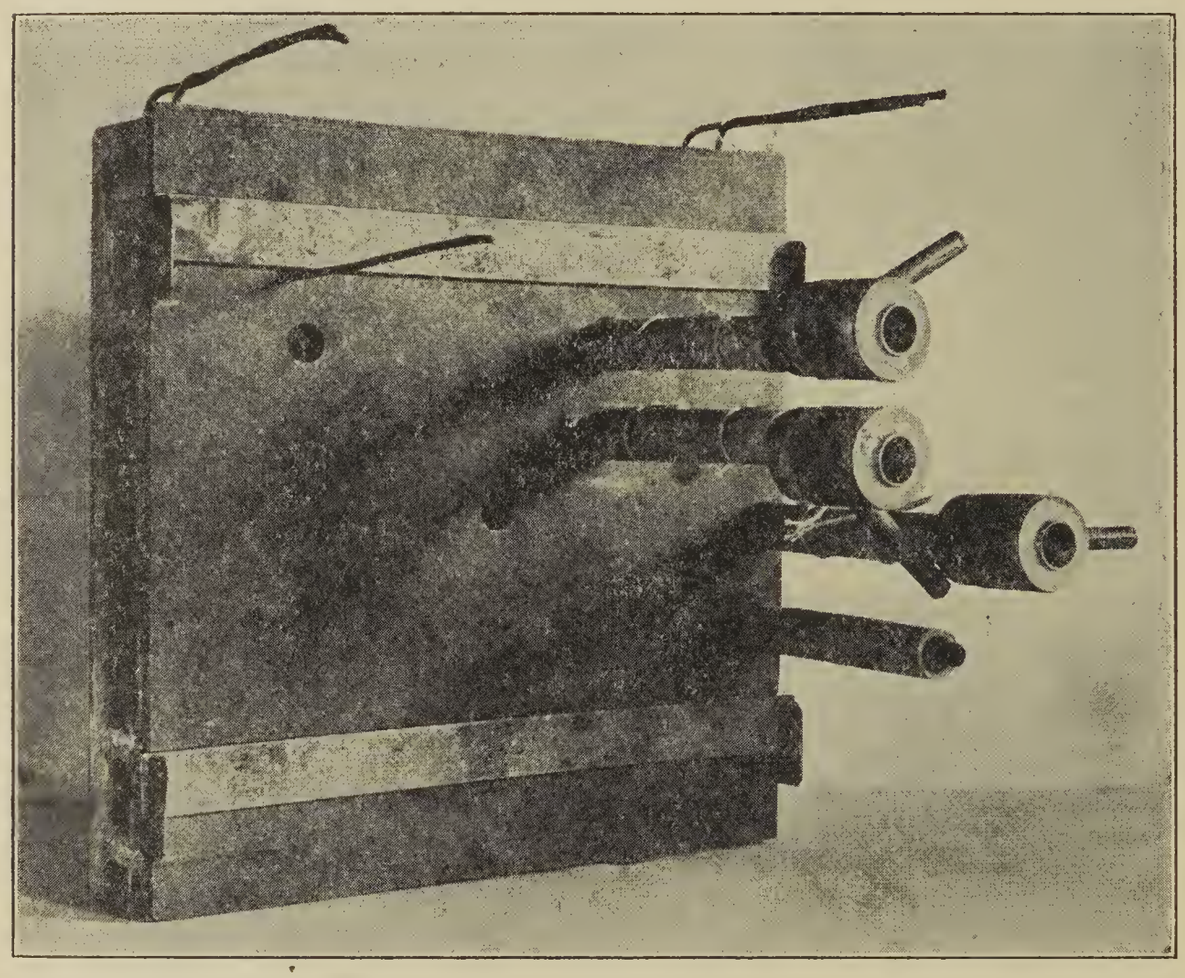

Fig. 5.

diaphragm without seriously interfering with the circulation of the water. The space between the two compartments of the calorimeter, amounting to 1/32 inch (0.8 mm.) is filled with a layer of blotting paper or with three layers of heavy detail paper. When in use the entire face of both compartments is covered with a layer of cork linoleum ¼ inch (0.6 cm.) thick, and the sections of the copper tubing leading from the calorimeter to the temperature jackets are covered with two thicknesses of rubber

tubing. Reference to Figs. 4, 5, and 6, will make clear the construction of the calorimeter and the arrangement of its various parts. Water is delivered to the inlet tubes of each compartment through a rubber tube, which is connected to a ¼-inch (0.6 cm.) pet-cock. Since all of the work described herein was done during the summer vacation, when the water supply of the building was not being used for any other purpose, it was unnecessary to adopt special means for maintaining a constant head of water in the inlet tubes of the calorimeter. The pet-cocks were therefore connected directly to the laboratory supply pipe.

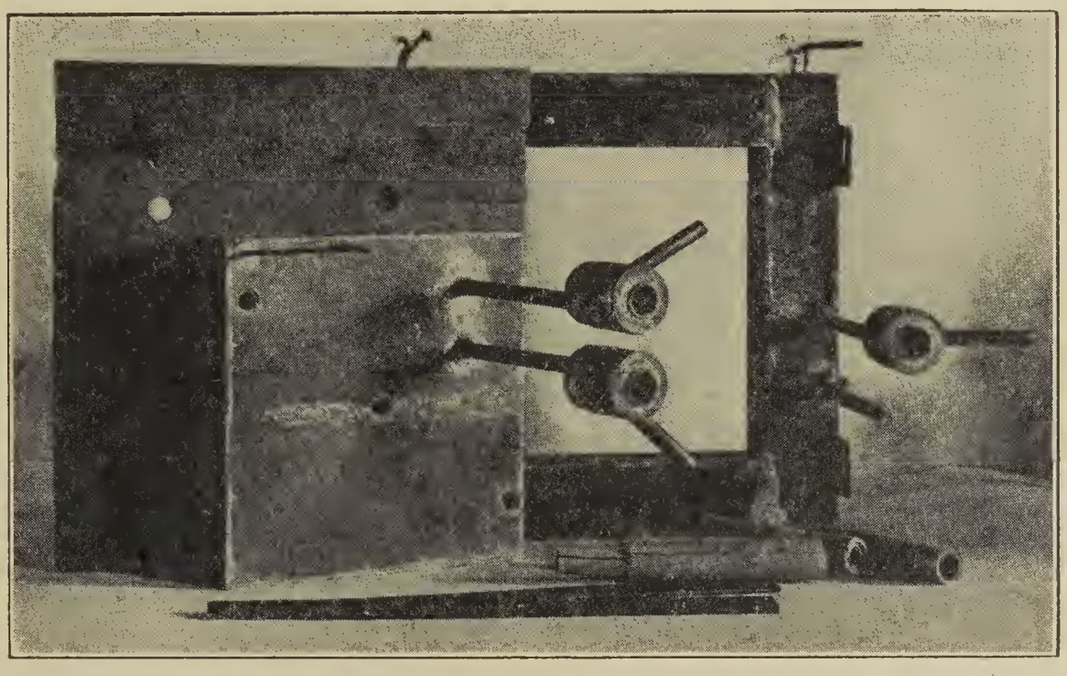

Fig. 6.

Aside from the consideration of heat exchange between the sides of an unprotected calorimeter and the surroundings, is it necessary to recognize the fact that when a cold water-jacket is applied to a heated surface, the area of which is greater than that of the jacket, the temperature of the part of the surface in contact with the jacket becomes lower than that of the surrounding surface, which remains exposed to the air. Consequently the lines of heat-flow are deflected, and heat flows to the margin of the area in contact with the jacket from the surrounding material as well as from the points within the wall that are directly opposite the jacket. The outside compartment of a calorimeter constructed as above described is the one that receives this heat from the surrounding portions of the wall, while all of the heat received

from the wall by the inner compartment flows through the brick in lines normal to the surface of the wall. Such, at any rate, is the assumption made in these experiments. In other words, it is assumed that all of the heat that leaves the wall through the 64 square inches (413 sq. cm.) of surface in contact with the inner compartment of the calorimeter enters the wall at the other side through an equal and opposite area. By operating both compartments of the calorimeter under the same temperature conditions, which is accomplished by regulating the flow of water through the outer compartment so that the temperature of the outflows from both are the same, the sides of the inner compartment are effectively protected against heat exchange with the surroundings. The water enters both compartments at the same

NOTE: Junctions marked *a* passed through one rubber stopper, which was inserted in the temperature-jacket on the inlet tube of the inner compartment.

Junctions marked *b* were inserted into the temperature jacket on the outlet tube of the inner compartment.

Junctions marked *c* were inserted into the temperature jacket on the outlet tube of the outer compartment.

Junctions marked *d* were carried in small glass tubes bound closely together, thus insuring that differences in temperature did not arise between these junctions.

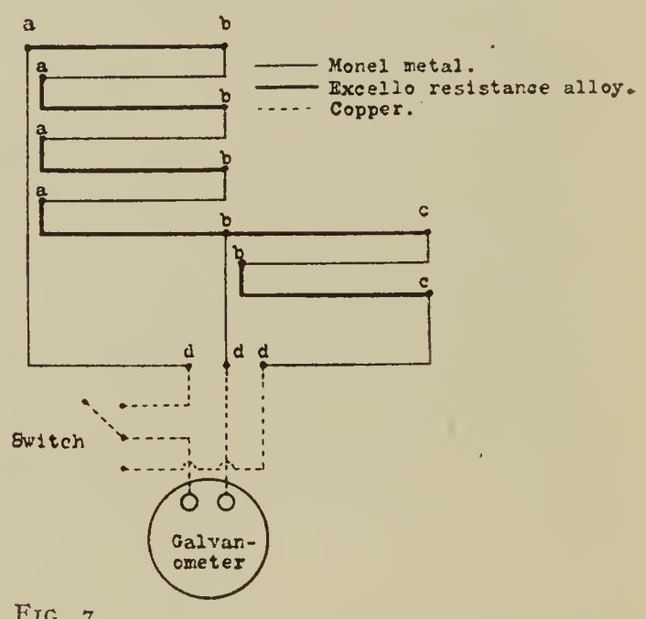

FIG. 7.

temperature since it comes to each from the same source, and it is possible to maintain the temperature of the outflows practically equal. During a test the difference is not permitted to become greater than 0.2° C. When the inner compartment is thus protected it is safe to assume that it receives heat from two sources only, from the heated brick surface and from the air in contact with the linoleum cover. The conductivity of the linoleum under these conditions is readily determined and may be allowed for, as will be explained later. The considerations stated above are chief among those that caused the selection of the double compartment type of calorimeter for use in these experiments.

The rise in temperature of the water flowing through the inner compartment and the difference in temperature of the outflows from the two compartments are measured by means of thermocouples and a sensitive galvanometer. The arrangement of the thermocouples and galvanometer is shown by the diagram, Fig. 7. The thermocouples consist of wires of Monel metal and "Excello" resistance alloy. The galvanometer used is a Leeds and Northrup instrument of the mirror type with a curved scale, and having an internal resistance of 609 ohms. Each group of junctions is carried by a rubber stopper through which the wires pass, being insulated from each other by the rubber and by small glass tubes. The rubber stoppers are inserted in the open tubes of the small cylindrical water-jackets to such a depth that the junctions are within ¼ inch (0.6 cm.) of the bottom of the tube. The volume of air space surrounding the junctions is thus reduced to a cylinder ⅝ inch in diameter by ½ inch (1.6 x 1.3 cm.) in length. The galvanometer will respond to a change in temperature of the water flowing through the temperature jackets within 15 seconds after the change occurs, and will give a constant reading within one minute. The method of calibrating these thermocouples was as follows: Two thermos bottles of one pint capacity were filled with water at slightly differing temperatures. The temperature of the water in each was determined to within 0.1° C. with a Beckmann thermometer graduated to 0.01° C. Then two sets of the junctions, each carried by its rubber stopper and protected by a test tube, were inserted into the necks of the bottles, one set of junctions being at the bottom of its test tube and at the center of each bottle. The terminals of the thermocouple circuit were connected with the galvanometer as shown in Fig. 7, and the couples were allowed to assume the temperature of the water in which they were immersed.

The difference in temperature between the water in the two bottles was registered by the galvanometer deflection. When the galvanometer reading became constant, the test tubes and couples were removed from the bottles and the temperature of the water in each was quickly determined with the Beckmann thermometer, the instrument being read to the nearest 0.01° C. Before inserting the thermometer into the bottle the temperature of bulb and stem of the instrument was brought to within 0.1° C. of that of the

water in the bottle by immersing the thermometer in mixtures of warm and cold water previously prepared. The temperature of the water in the thermos bottle could be predicted with certainty from the preliminary measurement. In this manner the error introduced into the final temperature measurements due to the heating or cooling of the bulb and stem of the thermometer by the water in the bottles was reduced to a minimum. Table I gives the calibration figures obtained by this method; the points are graphically represented in Fig. 8. These figures show the deflections produced by the two sets of junctions marked *a* and *b* in Fig. 7, when the junctions at *b* are at higher temperature than

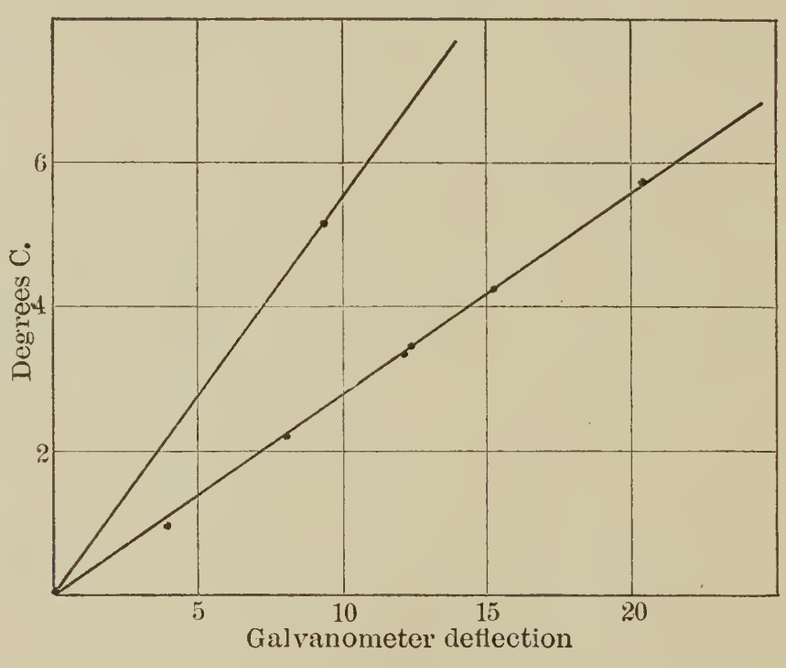

Fig. 8.

those at *a*. This is the condition under which the junctions are used in connection with the calorimeter.

Table I.

Temperature Difference Degrees C.	Galvanometer Deflections in Cm. on the Red Scale
0.99	3.8
2.20	8.0
3.38	12.2
3.46	12.3
4.27	15.2
5.73	20.3

Since the junction circuit *b-c* (Fig. 7) is used only to compare the temperature of the outflows from the calorimeter compartments, accurate calibration was not considered necessary and

only one point was taken. With 5.17 degrees difference in temperature this combination produced a deflection of 9.3 cm., which agrees well with the deflections produced by the other combination. The number of junctions in the second series being one half as great as in the first, the deflections produced should be one half for equal differences in temperature; the two straight lines shown in Fig. 8 illustrate this point. The relation between the galvanometer deflections and temperature differences is linear and may be expressed as follows:

For circuit *a-b*, 1 cm. galv. deflection = 0.279° C.
For circuit *b-c*, 1 cm. galv. deflection = 0.558° C.

These are the constants used in determining the rate of heat absorption by the calorimeter.

In the course of a conductivity determination the rate of flow of the water through the inner compartment of the calorimeter and the rise in temperature of this water during its passage through the compartment are measured. The product of the rate of flow expressed in grams per second into the rise in temperature expressed in degrees C. gives the rate of heat absorption by this compartment of the calorimeter expressed in gram calories per second. The heat thus determined comes from two sources, namely, the wall in contact with the calorimeter and the air in contact with the linoleum that covers the opposite face of the calorimeter. The air at this point is always at a higher temperature than the water within, and the amount of heat reaching the water from this source must be deducted from the total in order to find the true rate of heat flow through the wall. To determine the magnitude of this correction it was necessary to determine the thermal conductivity of the linoleum cover by means of such measurements as can be readily duplicated in the course of a regular conductivity test. It was found that, when the calorimeter was in its place in contact with the wall, the temperature of the air a short distance away from the surface of the linoleum was practically constnat from top to bottom of the calorimeter. The temperature variation between these points was not more than 2° C., when the temperatures were measured by a mercury thermometer placed with the bulb parallel to the surface and with the center of the bulb one inch distant from the surface.

The distance of the bulb from the surface affected the reading of the thermometer at the rate of about 0.5 degree for each ¼ inch (0.6 cm.), the temperature rising with increasing distance from the linoleum. From these figures it is apparent that if the temperature of the air in contact with the surface of the linoleum is determined with a mercury thermometer held near the center of the surface and at a distance of one inch from it, such a measurement can be duplicated with sufficient accuracy and without difficulty. The average temperature of the water within the calorimeter is readily obtained by deducting half the temperature rise from the actual temperature of the outflow, as indicated by a mercury thermometer. Therefore the conductivity of the cover of the calorimeter was determined in terms of the difference between the temperature of the air on the outside and the average temperature of the water on the inside, each of these temperatures being determined as above described.

To determine the conductivity of the linoleum the calorimeter was assembled as for a test, but in addition to the layer of linoleum over the face of the calorimeter a cover of the same material was placed in contact with the back side, it being held in position by two pieces of strap iron as was the cover on the opposite side. The entire apparatus was then mounted in a vertical position inside of a wooden box, the dimensions of which were 4 ft. high by 3 ft. by 3 ft. The position of the calorimeter was with its top edge about one inch below the top or lid of the box, while it was centrally placed with reference to the sides of the box. The interior of the box was accessible through one side, which was provided with a cover of corrugated paper. Holes were bored through the top of the box to admit two thermometers, one of which was suspended on each side of the calorimeter, the bulb being opposite the center of the side and one inch from the surface. An electric resistance heater was placed in the box, and by regulating the current through the heater by means of an external resistance any desired air temperature could be maintained within the box. The temperature rise of the water and the rate of flow through the inner compartment gave the rate of heat flow through the two linoleum-covered surfaces of this compartment. The temperature of the outflow from the outer compartment was kept within 0.2 degree of that from the inner

compartment. With a given current through the heating coil, the box was closed and the air temperature was allowed to rise until the maximum was attained. When the air temperature became constant, as measured by the two thermometers, and when the rise in temperature of the water became constant, the two were recorded together with the temperature of the outflowing water. The rate of flow of the water through the inner compartment was determined by catching the discharge in a tub and weighing it at the end of 15 minutes. The total heat flow thus determined

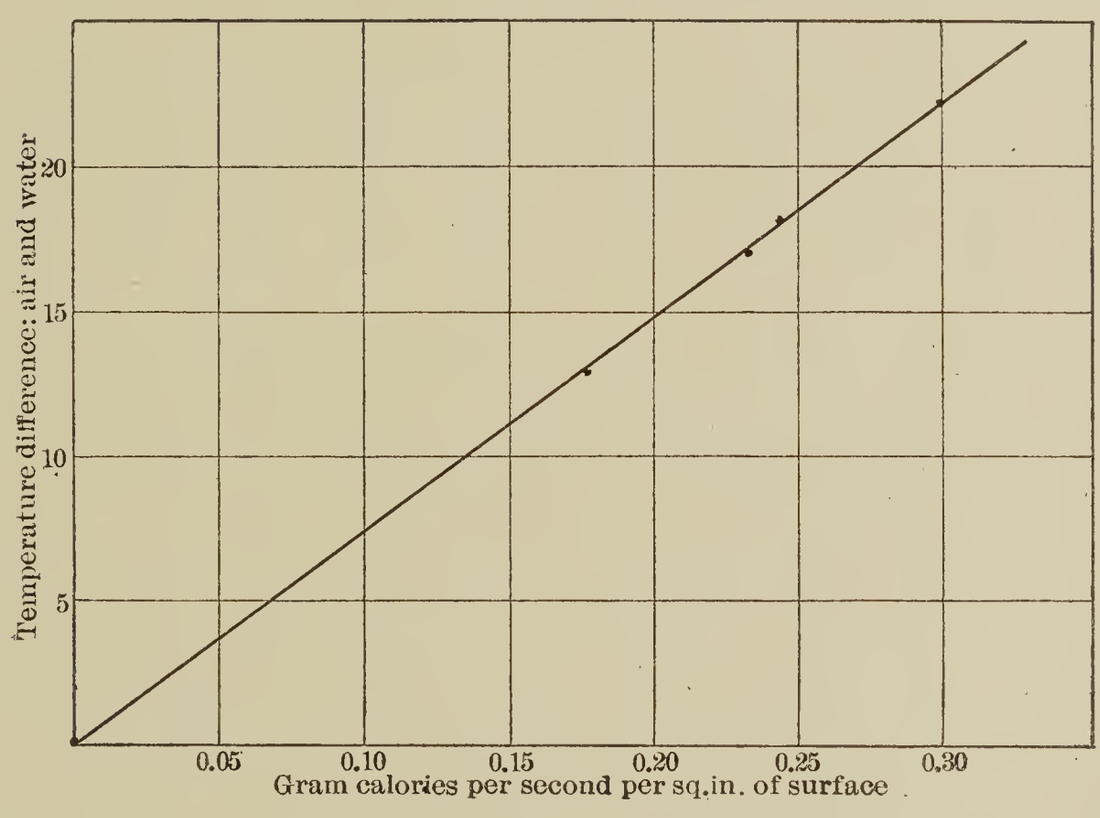

FIG. 9.

was that which passed through the two linoleum-covered faces of the inner compartment; the area of each of these is 64 square inches (413 sq. cm.). Hence the total rate of heat flow determined by such a test divided by 128 gives the rate of heat flow through one square inch of the linoleum-covered surface. In this method of interpreting the results the heat flow through the rubber covers of the copper tubes leading from the temperature jackets to the calorimeter is neglected. Table II gives the results of these tests; in Fig. 9 the results are graphically represented. It will be noted that the points fall practically on a straight line, which has been drawn through the origin. Theoretically this line

should cross the axis of abscissas slightly to the right of the origin on account of the heat generated by frictional resistance to the passage of the water through the calorimeter and its connections. The heat thus generated could be calculated from the rate of flow of the water and the loss of head in passing through the calorimeter. However, no attempt was made to measure the latter quantity, because the heat resulting from friction is necessarily small, and it is considered sufficiently accurate to draw the line through the origin as has been done in Fig. 9.

TABLE II.

Temp. Air		Temp. W.	Temp. Rise W.		Water Flow		Temp. Diff.	Calories per Sec.	
A	B	Out	Galv.	Deg. C.	lb. min.	g. sec.	Air-Water	Total	Sq. In.
31.0	32.0	19.0	2.80	0.778	3.82	28.8	12.9	22.5	0.176
35.0	36.0	19.0	3.80	1.06	3.70	28.0	17.0	29.6	0.232
37.0	37.0	19.5	4.00	1.11	3.70	28.0	18.1	31.1	0.243
41.0	41.0	19.5	4.90	1.36	3.70	28.0	22.2	38.1	0.298

In order to make clear the method of conducting a test to determine the conductivity of a refractory, a complete description of the operations involved will be given. Assuming that the wall has been constructed and dried as previously described, a fire is started in the furnace at about 6:00 A. M. As rapidly as possible the furnace is filled with the sized by-product coke that is used as a fuel. By 9:00 A. M. the bed of coke should be ignited from bottom to top, and the wall should be completely warmed through. At about 10:00 A. M. the calorimeter is placed in its position against the wall, and the corner made by the outer sides of the calorimeter and the surface of the wall is filled with asbestos fibre pulp, made by soaking scraps of asbestos paper in water. The purpose of filling this corner is to prevent the formation of air currents between the calorimeter and the brick in places where their contact is not sufficiently close. After the application of the calorimeter to the wall several hours are required to bring about uniform conditions. During this time the fire is urged, and the rate of flow of the water through the outer compartment is regulated in order to equalize the temperatures of the outflows. When the wall is so uniformly heated that the pyrometer inserted to the full depth of each of the three holes shows a variation of only 20 to 30 degrees in temperature from one hole to the next, the quantitative part of the test is started. To produce this con-

dition careful firing is required, and it is usually not possible to begin the quantitative part of the determination before 2:00 or 3:00 P. M.; in some cases the test cannot be started before 5:00 P. M. When uniform temperature conditions are obtained, the water from the inner compartment of the calorimeter is deflected into a galvanized iron tub, and readings are taken at five-minute intervals as follows: The temperature rise of the water flowing through the inner compartment is determined by reading the galvanometer deflection produced by the thermocouple circuit that measures this difference in temperature. In the same manner the difference in temperature between the two outflows is determined. The temperature of the air one inch from the face of the calorimeter is noted, as is the temperature of the outflow from the calorimeter. If, at the time of several successive readings, the outflows differ in temperature by more than 0.2 degree, a change is made in the rate of flow through the outer compartment in order to correct this condition. In the intervals of time between these readings the temperature gradients from the back to the front of the wall are taken. The thermocouple is inserted into one of the holes to its full depth and allowed to remain there until the galvanometer reading becomes constant; the reading is then recorded and the couple is pulled out of the hole a distance of ½ inch (1.3 cm.) where it is allowed to remain until the galvanometer reading again becomes constant. Subsequent readings are taken after the junction has been moved back ½ inch (1.3 cm.) each time, until nine readings are taken in each hole, the first and last readings of each set being ¼ inch (0.6 cm.) from the hot side and ¼ inch (0.6 cm.) from the cold side of the wall, respectively. About thirty minutes time is usually required for taking the readings through each hole, and on this account the readings taken at five minute intervals are conducted over a period of 1½ hours. When all of the temperature gradients have been taken, the temperature of the deepest part of each hole is redetermined. If these temperatures have not changed by more than 20 or 30 degrees, the test is considered finished. If the temperature at the back of any hole has changed more than 30 degrees, the test is continued until these temperatures remain constant or practically so for a sufficient time to allow the taking of three complete temperature gradients.

All of the temperature measurements within the brick are made with a thermocouple of Pt and Pt with 10 percent Rh, which is connected through a resistance of 4,000 ohms to the Leeds and Northrup galvanometer. One wire of the couple passes through a small silica tube, while the other is bare. The couple was calibrated by comparing it with a carefully standardized junction at a number of temperatures. The temperature of the cold junction was maintained at 32.5 degrees during the comparison, that being the average temperature of the cold junction when the couple is in use at the furnace.

The method employed in determining the temperatures at various points within the brick is open to question, because, after the first or innermost temperature has been taken, the subsequent positions of the thermocouple are such as to expose it to radiation from the hot end of the hole. Heat is not only radiated from the hot end of the hole but also is conducted from this point by the air that fills the hole. Hence a point on the wall of one of these holes may be at a higher temperature than that of the body of the brick at the same depth from the surface and at some distance from the hole, and the thermo-junction placed at this point may record a temperature higher than that of the brick at the same depth, where there is no hole. While it was thought that the error from this source would be slight or even inappreciable on account of the small diameter of the hole, nevertheless a test was made to determine the effect of the open hole upon the pyrometer readings. Five pieces were cut from a clay crucible and carefully filed until each was ½ inch long by ⅛ inch in diameter (1.3 x 0.3 cm.) Then at the completion of a conductivity test on a fire-clay brick and while the calorimeter was still in contact with the wall, six temperature determinations were made in the center hole; the first measurement was taken at the back of the hole and the others were taken at intervals of ½ inch (1.3 cm). Following this, one of the clay pieces was inserted into the hole and pushed to the back, and the couple was inserted with the junction in contact with the end of the clay. It was allowed to remain in this position until the galvanometer deflection became constant, indicating that the clay and the thermocouple had been heated to the temperature of the brick. The reading was recorded, and the process was repeated until all of

the clay pieces had been inserted into the hole. This test gave the temperatures of six points in the hole spaced ½ inch (1.3 cm.) apart as indicated by the pyrometer when the space between the junction and the end of the hole was open, and the temperatures of the same points as indicated by the pyrometer when the space between the junction and the end of the hole was filled with tightly fitting pieces of burnt fire-clay. The results are shown in Table III. The readings with the clay pieces in front of the junction and those without them show no consistent variation, and in view of this fact it seems safe to conclude that the course of the temperature gradient through the brick is determined by the method employed with as great exactness as is warranted by the heterogeneous composition of nearly all brick.

TABLE III.

Distance in Brick Inches	Open Hole		Hole Closed with Pieces of Clay	
	Galv. Def'n	Temp. C.	Galv. Def'n	Temp. C.
4.25	21.3	945	21.3	945
3.75	19.0	875	18.8	870
3.25	16.8	800	16.8	800
2.75	14.5	720	14.7	725
2.25	12.1	625	12.1	625
1.75	9.6	520	9.5	515

The time consumed in making the above measurements was about 25 minutes, and during this time the temperatures at the backs of the two adjacent holes did not vary more than 10 degrees, indicating that the temperature conditions throughout the wall were constant.

The results of tests on four types of refractories are given below. The kinds of brick tested were first quality fire-clay brick, silica brick with clay bond, silica brick with lime bond, and magnesite brick. All of the above were manufactured by the Harbison-Walker Refractories Co., Pittsburgh, Pa., and the writer wishes to acknowledge the kindness of the manufacturers in providing the samples used in these tests. Table IV gives the names under which these types of brick are supplied to the trade together with other information concerning their properties. The analyses were kindly provided by the manufacturer; they represent the average compositions of the various materials. The apparent densities were determined by the writer on the lots of brick submitted for these tests.

TABLE IV.

Percent	Woodland	Quartzite	Star Silica	Magnesite
SiO_2	52.93	73.91	95.85	2.50
Al_2O_3	42.69	22.87	0.88	0.50
Fe_2O_3	1.98	1.48	0.79	7.00
CaO	0.33	0.29	1.80	2.75
MgO	0.38	0.31	0.14	86.50
Alkalies	1.55	1.20	0.39	....
Loss on ignition	....	....	....	0.10
Apparent density	1.91	1.91	1.56	2.46

The Woodland brick is made entirely of fire-clay from the conglomerate vein of clay in Pennsylvania, which at the point of manufacture contains both flint clay and the plastic clay necessary for bond. This brick is used largely in malleable furnaces, heating furnaces, and in general mill work where refractory fire-clay brick are required.

The Quartzite brick is made from a mixture of ganister rock with Pennsylvania flint and bond clays. This type of brick was formerly much used in by-product coke oven construction, but during the past few years the amount so used has greatly diminished, on account of the increased use of the lime-bond silica brick for this purpose.

The Star Silica brick are made from high grade Pennsylvania ganister rock, lime being used as a bonding agent. This type of brick is commonly used in open-hearth steel furnaces, for the roofs of copper reverberatory furnaces, for by-product coke ovens, in the construction of glass tanks, etc.

The Magnesite brick are made from the dead-burned material. They are dense and hard, and are representative of the type that is commonly used for the construction of open-hearth bottoms, for the lining of copper converters, and for lining other types of metallurgical furnaces where basic material is needed.

CONDUCTIVITY OF FIRST QUALITY WOODLAND FIRE-CLAY BRICK.

Test No. 1. Fire was started in the furnace at 7:00 A. M. The calorimeter was attached to the wall at 2:00 P. M. Readings were taken from 4:25 to 5:25 P. M.

Temperature rise of the water flowing through the inner compartment: Galvanometer readings were taken at five-minute

intervals beginning at 4.25; the deflections noted were as follows: 19.1, 19.8, 20.3, 20.1, 20.0, 20.2, 20.7, 20.7, 20.6, 20.3, 21.3, 20.9, 20.6.

Average of these readings = 20.4.

Average temperature rise of water = 20.4 x 0.279 = 5.69° C.

Amount of water through inner compartment of calorimeter: Water during 1 hr. = 143.0 — 12.5 (weight of tub) = 130.5 lb.

Temperature of water leaving both compartments: A mercury thermometer with its bulb held in the outflow from the outer compartment was read at five-minute intervals during the test. The average of the temperatures recorded is 25.5° C.

Temperature of the air one inch from the linoleum cover of the calorimeter: Readings were taken at five-minute intervals during the test. The average of the temperatures recorded is 37.0° C.

Temperature gradients through the brick wall: The temperature of the cold junction of the pyrometer was 31 to 34° C.

Distance in brick, inches	*a* Upper hole	*b* Center hole	*c* Lower hole	Ave. Galv. Reading	Temperature deg. C.
0.25	2.3	2.3	2.5	2.4	175
0.75	4.5	4.7	5.2	4.6	285
1.25	6.3	6.7	7.5	6.8	390
1.75	8.6	8.9	9.5	9.0	490
2.25	10.8	11.2	11.5	11.2	590
2.75	13.2	13.4	13.9	13.5	680
3.25	15.5	15.9	16.6	16.0	775
3.75	18.0	18.4	18.9	18.4	855
4.25	20.5	20.6	21.0	20.7	925

Time of taking the above readings: Those under *a* were taken between 4:15 and 4:35 P. M.; those under *b* were taken between 4:40 and 5:00 P. M.; those under *c* were taken between 5:10 and 5:25 P. M. At 5:30 the temperatures at the backs of all of the holes were measured with the following results: *a*, galvanometer deflection = 20.7; *b*, galvanometer deflection = 20.5; *c*, galvanometer deflection = 20.8. These measurements show practically no change in temperature at the backs of the holes.

The mean conductivity of the brick between the two temperature extremes is calculated from the above data as follows:

The rate of total heat absorption by the inner compartment of the calorimeter =

$$\frac{131 \text{ lb. of water} \times 454 \text{ g.} \times 5.69 \text{ deg.}}{1 \text{ hr.} \times 3{,}600 \text{ sec.} \times 64 \text{ sq. in. (area of cal. surface)}} = 1.47 \text{ g. cal.}$$

per sq. in. per second. This figure represents the total heat that enters the calorimeter each second from one square inch of the wall and through one square inch of the linoleum-covered surface exposed to the air. The heat from the wall is found by

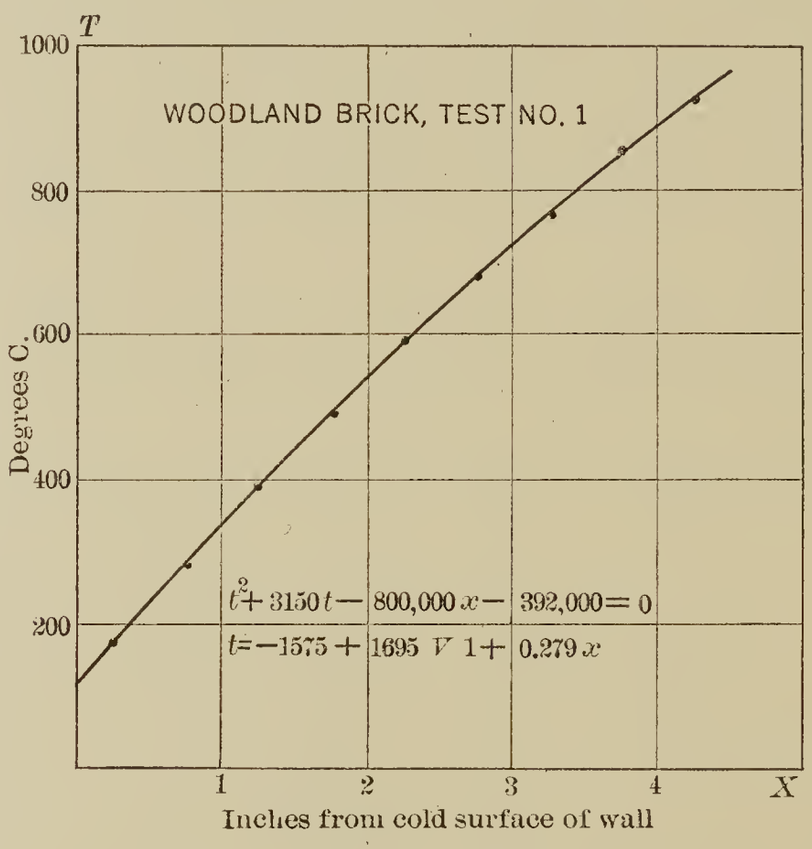

FIG. 10 (V in above cut should be $\sqrt{}$)

deducting from the total heat that heat which enters through the linoleum cover, the latter being estimated as follows: The temperature of the outflowing water during the test was 25.5° C. (average). Deduct from this one-half the temperature rise of the water flowing through the calorimeter, 25.5 — 2.9 = 22.6° C., which is the average temperature of the water inside the calorimeter. The average temperature of the air one inch from the surface of the linoleum cover during the test was 37.0° C. The difference in temperature between the air outside and the water inside is 37.0 — 22.6 = 14.4° C. Fig. 9 shows the rate of heat flow through the linoleum cover of the calorimeter under these

conditions to be 0.20 g. cal. per sec. per sq. in. The heat from each square inch of the wall is therefore 1.47 — 0.20 = 1.27 g. cal. per sec. The temperature gradient through the wall during this test is graphically shown in Fig. 10, distances from the cool side of the wall being plotted as abscissas, temperatures as ordinates. Extending the line of determined temperatures at each end as has been done in the figure, shows the temperature of the surfaces to have been 120° and 965° C., on the cool and hot sides respectively. The mean conductivity between these extremes of temperature is given by the equation

$$\text{conductivity} = \frac{\text{(heat flow per sq. in. per sec.)} \times \text{(thickness of wall, inches)}}{\text{(difference in temperature between faces of wall)}}$$

or

$$K = \frac{H\,x}{T_2 - T_1}$$

in which the conductivity is expressed in g. cal. per sec. through a cube with one-inch edge when the difference in temperature between opposite faces is 1° C. In the case under consideration

$$K = \frac{1.27 \times 4.5}{965 - 120} = 0.00676$$

which is the mean conductivity of this material between the temperatures 120° and 965° C.

The record given above and the explanation of the method of calculation will serve to illustrate the procedure followed in each case. Records of subsequent tests will be given in briefer form, and the calculation in each case will be made without further explanation.

Test No. 2. Fire was started in furnace at 6:00 A. M. Calorimeter was attached to wall at 10:00 A. M. Readings were taken from 1:40 P. M. to 3:10 P. M. Total time of test = 1.5 hr.

Temperature rise of water flowing through inner compartment: Average galvanometer deflection from 19 readings at five-minute intervals = 21.3. Temp. rise = 21.3 × 0.279 = 5.94° C.

Amount of water through inner compartment: During first half hour 67.25 lb., second half hour 67.75, third half hour 67.75. Total water in 1.5 hours = 202.75 lb.

Temperature of water leaving both compartments: Average of 19 determinations = 24.5° C.

Temperature of air one inch from face of calorimeter: Average of 19 determinations = 38.0° C.

Temperature gradients through the brick wall: The temperature of the cold junction was 30° to 33° C.

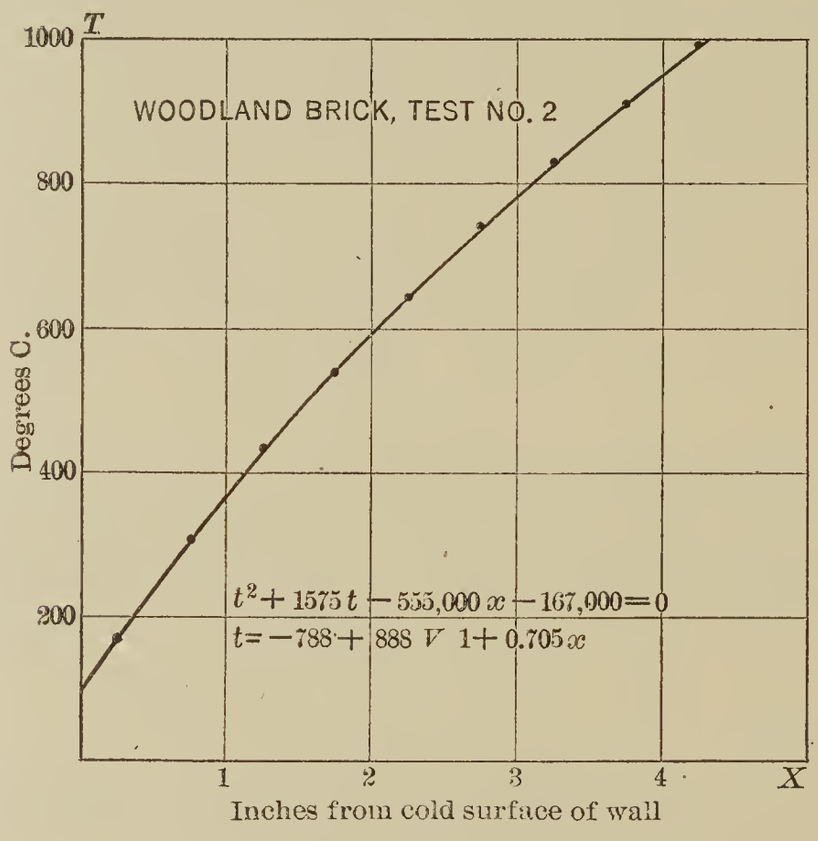

FIG. 11 (V in above cut should be $\sqrt{}$)

Distance in brick, inches	*a* Upper hole	*b* Center hole	*c* Lower hole	Ave. Galv. Reading	Temperature deg. C.
0.25	2.2	2.4	2.4	2.3	170
0.75	4.7	5.0	5.3	5.0	305
1.25	7.6	7.6	7.8	7.7	435
1.75	10.0	10.0	10.2	10.1	540
2.25	12.5	12.2	12.6	12.4	640
2.75	15.1	14.7	15.3	15.0	740
3.25	17.8	17.2	17.8	17.6	830
3.75	20.6	19.7	20.4	20.2	910
4.25	23.1	22.2	23.3	22.9	995

Time at which the above readings were taken: *a* from 1:45 to 2:05, *b* from 2:10 to 2:30, *c* from 2:30 to 2:50. At 3:05 the galvanometer deflections with the junction at the backs of the holes were, $a = 23.4$, $b = 22.6$, and $c = 23.3$.

The above figures have been plotted to scale in Fig. 11. The temperatures of the surfaces of the brick are 100° and 1025° C.

Rate of heat flow into the inner compartment of the calorimeter from 1 sq. in. of wall surface and through 1 sq. in. of the linoleum cover

$$\frac{203 \text{ lb.} \times 454 \text{ g.} \times 5.94 \text{ deg.}}{1.5 \text{ hr.} \times 3600 \text{ sec.} \times 64 \text{ sq. in.}} = 1.59 \text{ g. cal. per sec.}$$

Rate of heat flow through linoleum cover: Temperature difference between air outside of calorimeter and water inside = 38.0 — (24.5 — 3.0) = 16.5° C. Fig. 9 shows the rate to be 0.22 g. cal. per sec. per sq. in.

Heat flow from wall to calorimeter = 1.59 — 0.22 = 1.37 g. cal. per sec. per sq. in.

Mean conductivity of brick between 100° and 1025° C.:

$$K = \frac{H\,x}{T_2 - T_1} = \frac{1.37 \times 4.5}{1025 - 100} =$$

0.00666 g. cal. per sec. per inch cube per C. degree.

Test No. 3. In this test the wall was covered with a slab of asbestos wood 24 inches square by 1½ inches thick (61 x 61 x 3.8 cm.), which was held in close contact with the surface of the test wall and to the outer side of which the calorimeter was attached. By covering the wall in this manner the mean temperature of the brick during the test was increased, and the third test was thus made under conditions somewhat different from those existing during the two previous determinations.

Fire was started in the furnace at 6:00 A. M. Calorimeter and asbestos wood were attached to wall at 10:00 A. M. Readings were taken from 4:30 to 6:00 P. M. Total time of test = 1.5 hr.

Temperature rise of water flowing through inner compartment: Average galvanometer deflection from 19 readings at five-minute intervals = 15.9. Temp. rise = 15.9 x 0.279 = 4.44° C.

Amount of water through inner compartment: During first half hour 65.75 lb., second half hour 64.0 lb., third half hour 62.5 lb. Total water in 1.5 hours = 192.25 lb.

Temperature of water leaving both compartments: Average of 19 determinations = 25.5° C.

Temperature of air one inch from face of calorimeter: Average of 19 determinations = 37.0° C.

Temperature gradients through the brick wall. Cold junction temperature was 31° to 34° C.

Distance in brick, inches	*a* Upper hole	*b* Center hole	*c* Lower hole	Ave. Galv. Reading	Temperature deg. C.
0.25	7.7	7.7	8.2	7.9	440
0.75	9.6	9.6	10.1	9.8	530
1.25	11.6	11.4	11.9	11.6	605
1.75	13.2	13.0	13.5	13.2	670
2.25	15.0	14.9	14.9	14.9	735
2.75	16.8	16.5	16.8	16.7	795
3.25	18.7	18.2	18.8	18.6	860
3.75	20.5	20.0	20.6	20.4	920
4.25	22.2	21.4	22.6	22.1	970

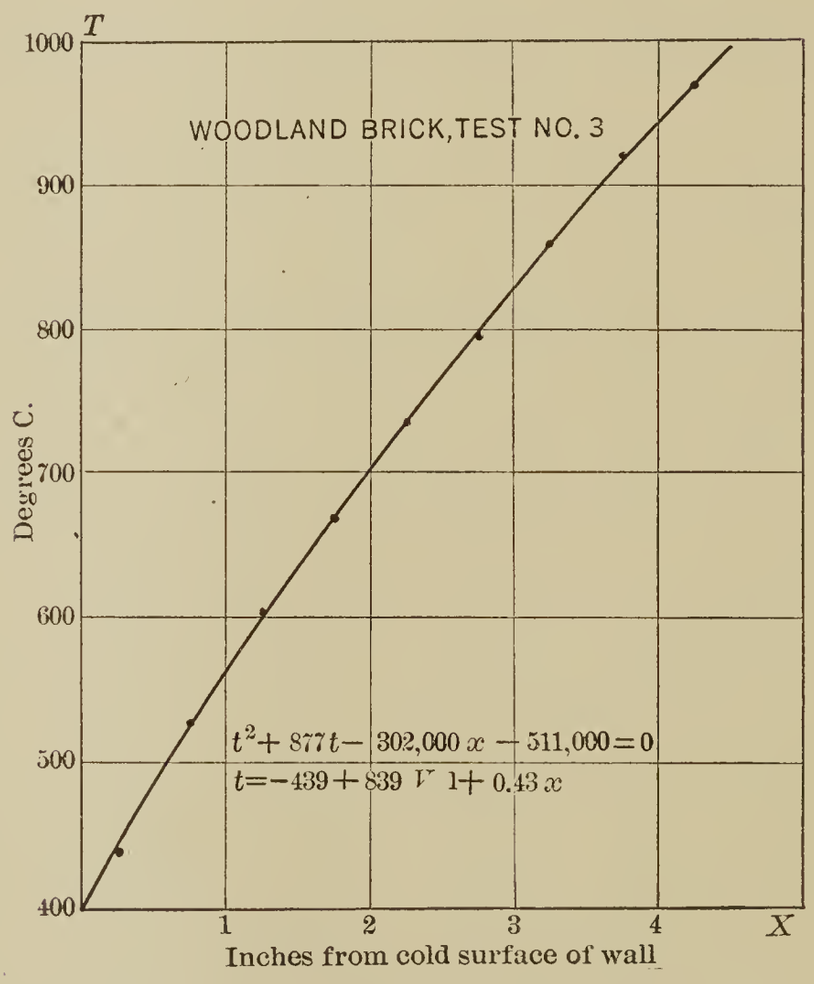

FIG. 12 (V in above cut should be $\sqrt{}$)

Time at which the above readings were taken: *a* from 4:30 to 4:50, *b* from 5:00 to 5:35, *c* from 5:45 to 6:10. At 6:15 the galvanometer deflections with the junctions at the backs of the holes were, $a = 22.4$, $b = 21.8$, $c = 22.5$.

The above figures have been plotted to scale in Fig. 12. The temperatures of the surfaces of the brick are 400° and 995° C.

Rate of heat flow into the inner compartment of the calorimeter from 1 sq. in. of wall surface and through 1 sq. in. of the linoleum cover =

$$\frac{192 \text{ lb.} \times 454 \text{ g.} \times 4.44^\circ \text{ C.}}{1.5 \text{ hr.} \times 3600 \text{ sec.} \times 64 \text{ sq. in.}} = 1.12 \text{ g. cal. per sec.}$$

Rate of heat flow through linoleum cover: Temperature difference between air outside of calorimeter and water inside = 37.0 — (25.5 — 2.2) = 13.7. Fig. 9 shows the rate to be 0.19 g. cal. per sec. per sq. in.

Heat flow from wall to calorimeter = 1.12 — 0.19 = 0.93 g. cal. per sec. per sq. in.

Mean heat conductivity of the brick between 400° and 995° C.

$$K = \frac{H\,x}{T_2 - T_1} = \frac{0.93 \times 4.5}{995 - 400} =$$

0.00704 g. cal. per sec. per inch cube per C. degree.

CONDUCTIVITY OF QUARTZITE BRICK.

Test No. 1. Fire was started in furnace at 6:00 A. M. Calorimeter was attached to wall at 10:00 A. M. Readings were taken from 2:05 to 4:05 P. M. Total time of test = 2.0 hr.

Temperature rise of water flowing through inner compartment: Average galvanometer deflection from 25 readings taken at five-minute intervals = 19.8. Temp. rise = 19.8 x 0.279 = 5.52° C.

Amount of water through inner compartment: During first half hour 65.5 lb., second half hour 65.5 lb., third half hour 67.5 lb., fourth half hour 67.5 lb. Total water in 2.0 hours = 265.5 lb.

Temperature of water leaving both compartments: Average of 25 determinations = 22.5° C.

Temperature of air one inch from face of calorimeter: Average of 25 determinations = 34.0° C.

Temperature gradients through the brick wall. Cold junction temperature was 30° to 34° C.

Distance in brick, inches	*a* Upper hole	*b* Center hole	*c* Lower hole	Ave. Galv. Reading	Temperature deg. C.
0.25	2.1	2.0	2.0	2.0	155
0.75	4.3	4.3	4.2	4.3	270
1.25	6.5	6.5	6.3	6.4	373
1.75	8.6	8.5	8.6	8.6	475
2.25	10.8	10.7	10.9	10.8	573
2.75	13.0	13.0	13.0	13.0	663
3.25	15.3	15.0	15.2	15.2	745
3.75	17.6	17.3	17.3	17.4	823
4.25	19.6	19.5	19.3	19.5	890

Time at which the above readings were taken: *a* from 3:00 to 3:25, *b* from 2:30 to 3:00, *c* from 2:05 to 2:25. Between 3:45 and 4:00 the galvanometer deflections with the junctions at the backs of the holes were, $a = 19.1$, $b = 19.2$, $c = 19.4$.

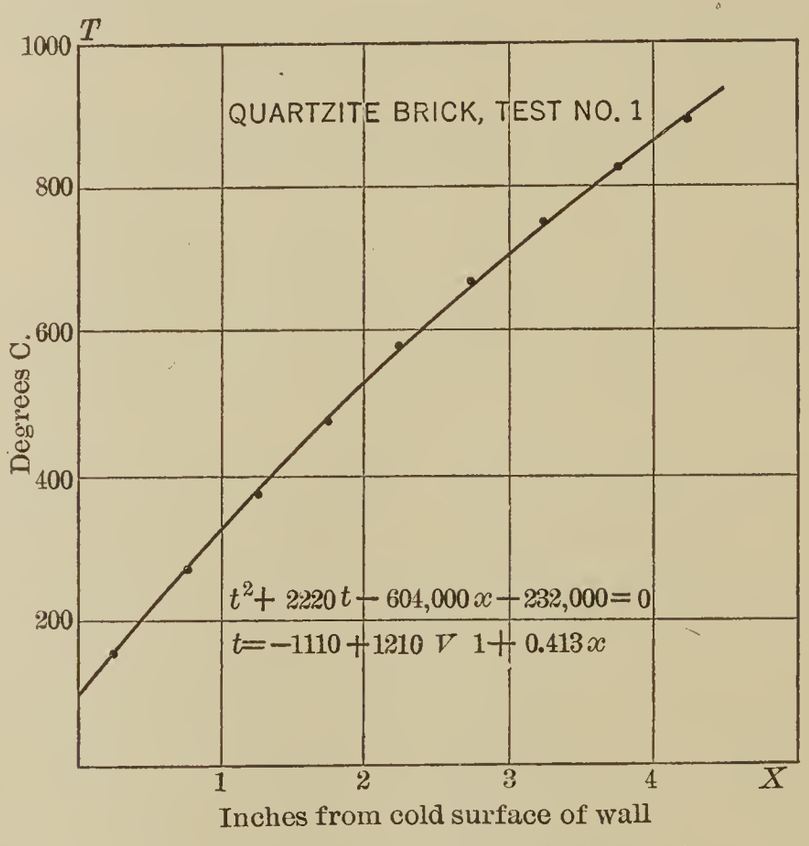

FIG. 13 (V in above cut should be $\sqrt{}$)

The above figures have been plotted to scale in Fig. 13. The temperatures of the surfaces of the brick are 100° and 935° C.

Rate of heat flow into the inner compartment of the calorimeter from 1 sq. in. of wall surface and through 1 sq. in. of the linoleum cover =

$$\frac{266 \text{ lb.} \times 454 \text{ g.} \times 5.52 \text{ deg.}}{2.0 \text{ hr.} \times 3600 \text{ sec.} \times 64 \text{ sq. in.}} = 1.45 \text{ g. cal. per sec.}$$

Rate of heat flow through linoleum cover: Temperature difference between air outside of calorimeter and water inside = 34.0 — (22.5 — 2.8) = 14.3° C. Fig. 9 shows the rate of flow to be 0.19 g. cal. per sec. per sq. in.

Heat flow from wall to calorimeter = 1.45 — 0.19 = 1.26 g. cal. per sec. per sq. in.

Mean heat conductivity of the brick between 100° and 935°,

$$K = \frac{H\,x}{T_2 - T_1} = \frac{1.26 \times 4.5}{935 - 100} =$$

0.00679 g. cal. per sec. per inch cube per C. degree.

Test No. 2. At the completion of test No. 1 the furnace fire was urged and additional air was supplied by directing the blast from a 16-inch electric fan into the draft holes at the back of the furnace. After two hours a second set of readings was taken from 6:00 to 6:30 P. M. Total time of test = 0.5 hr.

Temperature rise of water flowing through inner compartment of the calorimeter: Average galvanometer deflection from seven readings taken at five-minute intervals = 20.4.

Temp. rise = 20.4 × 0.279 = 5.69° C.

Amount of water through inner compartment: Total in 0.5 hr. = 67.0 lb.

Temperature of water leaving both compartments: Average of seven determinations = 22.5° C.

Temperature of air one inch from face of calorimeter. Average of seven determinations = 36.0° C.

Temperature gradients through the brick wall. Cold junction temperature was 32° to 35° C.

Distance in brick, inches	*a* Upper hole	*b* Center hole	*c* Lower hole	Ave. Galv. Reading	Temperature deg. C.
0.25	2.0	2.1	2.2	2.1	160
1.25	6.6	6.5	6.6	6.6	380
2.25	11.1	10.9	11.0	11.0	580
3.25	15.7	15.5	15.6	15.6	760
4.25	20.6	20.2	20.5	20.4	920

All of the above readings were taken during the test, *i. e.*, between 6:00 and 6:30 P. M.

The above figures have been plotted to scale in Fig. 14. The temperatures at the surfaces of the brick are 100° and 960° C.

Rate of heat flow into inner compartment of calorimeter from 1 sq. in of wall surface and through 1 sq. in. of the linoleum cover =

$$\frac{67.0 \text{ lb.} \times 454 \text{ g.} \times 5.69 \text{ deg.}}{0.5 \text{ hr.} \times 3600 \text{ sec.} \times 64. \text{ sq. in.}} = 1.50 \text{ g. cal. per sec.}$$

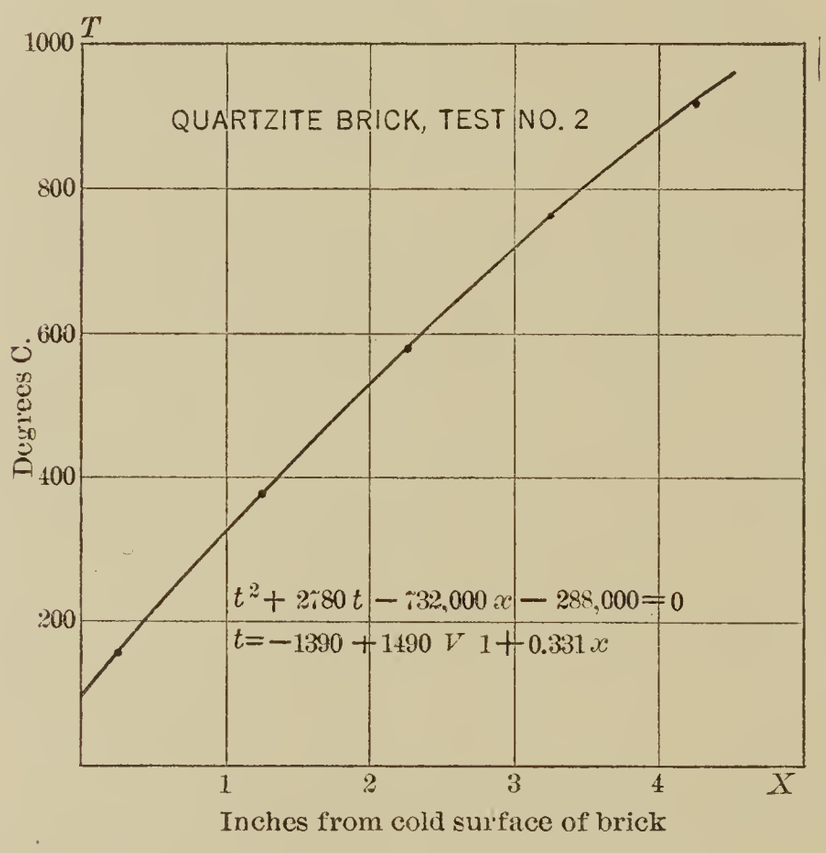

FIG. 14 (V in above cut should be $\sqrt{}$)

Rate of heat flow through linoleum cover: Temperature difference between air outside of calorimeter and water inside = 36.0 — (22.5 —2.8) = 16.3° C. Fig. 9 shows the rate to be 0.22 g. cal. per sec. per sq. in.

Rate of heat flow from wall to calorimeter = 1.50 — 0.22 = 1.28 g. cal. per sec. per sq. in.

Mean heat conductivity of the brick between 100° and 960° C,

$$K = \frac{H\,x}{T_2 - T_1} = \frac{1.28 \times 4.5}{960 - 100} =$$

0.00670 g. cal. per sec. per inch cube per C. degree.

CONDUCTIVITY OF STAR SILICA BRICK.

Owing to the fact that the furnace was fired too soon after the construction of the test wall the brick cracked badly on account of insufficient preliminary drying and it was found impossible to make more than one test on this material.

Fire was started in furnace at 6:00 A. M. Calorimeter was attached to wall at 10:00 A. M. Readings were taken from 3:20 to 4:50 P. M. Total time of test = 1.5 hr.

Temperature rise of water flowing through inner compartment: Average galvanometer deflection from 19 readings taken at five-minute intervals = 17.6. Temp. rise = 17.6 × 0.279 = 4.91° C.

Amount of water through inner compartment: During the first half hour 86.0 lb., second half hour 86.0 lb., third half hour 84.0 lb. Total water in 1.5 hr. = 256.0 lb.

Temperature of water leaving both compartments: Average of 19 determinations = 25.0° C.

Temperature of air one inch from face of calorimeter: Average of 19 determinations = 39.0° C.

Temperature gradients through brick wall. Cold junction temperature was 33° to 34° C.

Distance in brick, inches	*a* Upper hole	*b* Center hole	*c* Lower hole	Ave. Galv. Reading	Temperature deg. C.
0.25	2.2	2.2	2.0	2.1	160
0.75	4.6	4.6	4.5	4.6	285
1.25	6.7	6.5	6.5	6.6	380
1.75	8.6	8.6	8.7	8.6	475
2.25	10.6	10.6	10.6	10.6	565
2.75	12.6	12.7	12.6	12.6	645
3.25	14.7	14.7	14.8	14.7	725
3.75	17.1	16.9	17.0	17.0	800
4.25	19.1	19.0	19.1	19.1	875

Time at which the above readings were taken: *a* from 3:20 to 3:50, *b* from 3:50 to 4:10, *c* from 4:10 to 4:30. Between 4:35 and 4:50 the galvanometer deflections with the junction at the backs of the holes were, *a* = 19.2, *b* = 18.9, *c* = 19.0.

The above figures have been plotted to scale in Fig. 15. The temperatures at the surfaces of the brick are 100° and 910° C.

Rate of heat flow into the inner compartment of calorimeter from 1 sq. in. of wall surface and through 1 sq. in. of the linoleum cover =

$$\frac{256 \text{ lb.} \times 454 \text{ g.} \times 4.91 \text{ deg.}}{1.5 \text{ hr.} \times 3600 \text{ sec.} \times 64 \text{ sq. in.}} = 1.65 \text{ g. cal. per sec.}$$

Rate of heat flow through linoleum cover: Temperature difference between air outside of calorimeter and water inside =

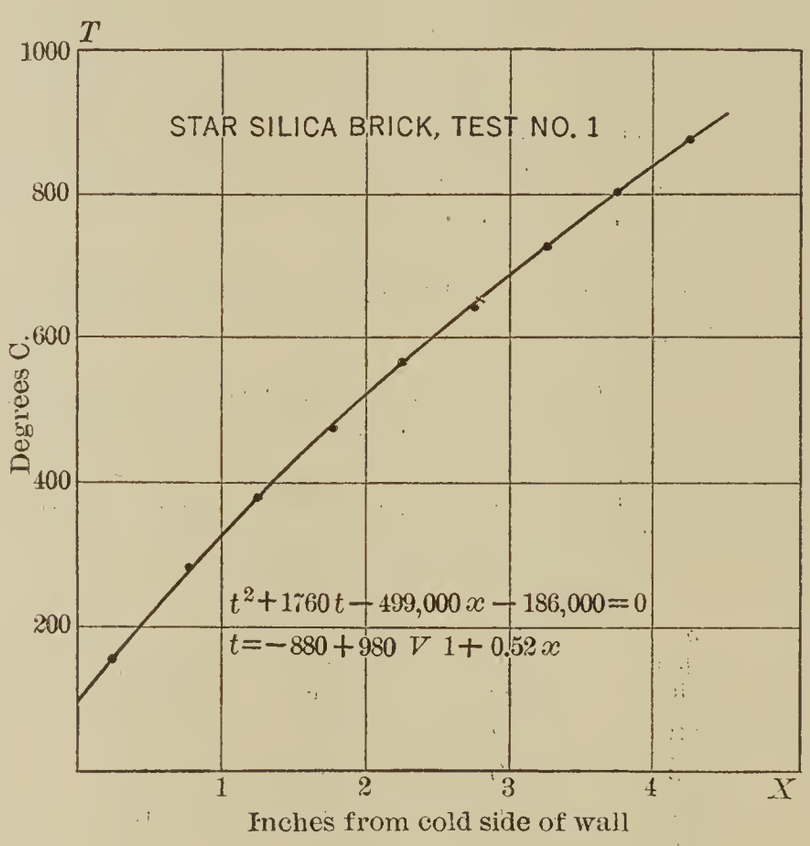

FIG. 15 (V in above cut should be $\sqrt{\ }$)

39.0 — (25.0 + 2.5) = 16.5° C. Fig. 9 shows the rate of heat flow to be 0.22 g. cal. per sec. per sq. in.

Rate of heat flow from wall to calorimeter = 1.65 — 0.22 = 1.43 g. cal. per sec. per sq. in.

Mean heat conductivity of the brick between 100° and 910° C.,

$$K = \frac{H\,x}{T_2 - T_1} = \frac{1.43 \times 4.5}{910 - 100} =$$

0.00794 g. cal. per sec. per inch cube per C. degree.

CONDUCTIVITY OF MAGNESITE BRICK.

Fire was started in furnace at 6:00 A. M. Calorimeter was attached to wall at 10:00 A. M. Owing to the high conductivity of the brick considerable difficulty was experienced in securing even a moderately high temperature on the hot side of the wall. By the use of forced draft from the electric fan it was possible to secure a temperature of about 850° C. at this point. Readings were taken from 5:00 to 6:30 P. M. Total time of test = 1.5 hr.

Temperature rise of water flowing through inner compartment: Average galvanometer deflection from 19 readings at five-minute intervals = 19.6. Temp. rise = 19.6 × 0.279 = 5.47° C.

Amount of water through inner compartment: During first quarter hour of test 88.0 lb., during third quarter hour 88.0 lb., fifth quarter hour 88.0 lb. Total water in 1.5 hr. = 528 lb.

Temperature of water leaving both compartments: Average of 19 determinations = 22.5° C.

Temperature of air one inch from face of calorimeter: Average of 19 determinations = 40.0° C.

Temperature gradients through brick wall. Cold junction temperature was 32° to 35° C.

Distance in brick, inches	*a* Upper hole	*b* Center hole	*c* Lower hole	Ave. Galv. Reading	Temperature deg. C.
0.25	5.4	5.0	5.5	5.3	320
0.75	8.0	8.0	7.8	7.9	445
1.25	9.2	9.1	9.0	9.1	495
1.75	10.4	10.3	10.1	10.3	550
2.25	11.3	11.5	11.2	11.3	595
2.75	12.5	12.6	12.4	12.5	645
3.25	14.1	14.0	13.9	14.0	700
3.75	15.4	15.6	15.2	15.4	750
4.25	16.9	16.8	16.6	16.8	800

Time at which the above readings were taken: *a* from 5:00 to 5:25, *b* from 5:25 to 5:45, *c* from 5:50 to 6:15. Between 6:20 and 6:30 the galvanometer deflections at the backs of the holes were, $a = 17.1$, $b = 17.0$, $c = 16.9$.

The above figures have been plotted to scale in Fig. 16. The temperature gradient in this case is unlike those obtained from the tests of the three other types of brick. From 800 deg. to 445 deg. the line is practically straight, indicating constant conductivity between these points. Below the latter temperature the curve makes a sharp bend downward, which, if the figures at

hand show the true temperature conditions within the brick, indicates a considerable and an abrupt change in the conductivity at this point. The reason for such a change in conductivity, assuming its existence, is not clear to the writer. On the other hand there appear no good reasons for doubting the accuracy of the temperature measurements that indicate this state of affairs. The agreement among the three sets of observations is good, and furthermore, by comparing this test with the others, it is possible to calculate approximately the temperature of the outer surface of the magnesite brick during the test, which calculated figure is in close agreement with the observations. The calculation is based on the following: The resistance to heat flow between the surface

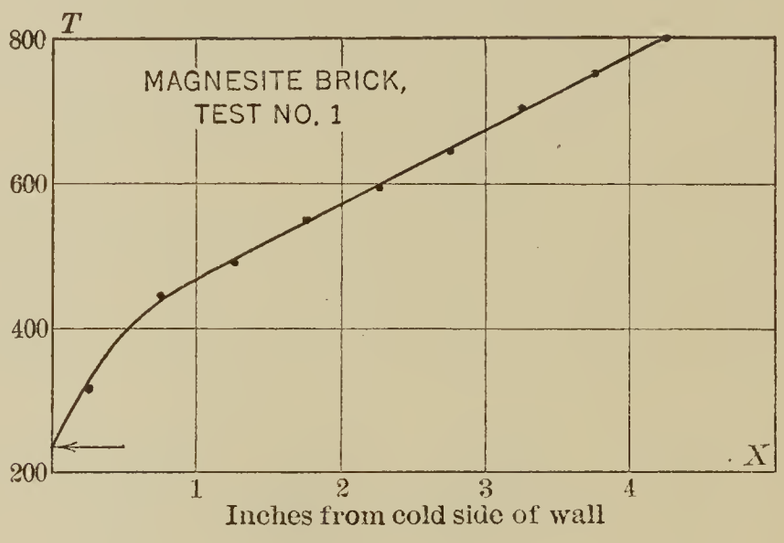

Fig. 16.

of the brick and the water in the calorimeter is the sum of the following component resistances: brick to air, air film, air to brass, brass, and brass to water. Of these the first two are the only ones that are likely to vary from one test to another, and, since the brick surface was in all cases painted with cement and the fit of the calorimeter to the wall was as close as possible in each case, it may be reasonably assumed that these two components of the total resistance were practically the same in all of the tests. Therefore it may be said that the total resistance to heat flow between the brick surface and the water in the calorimeter was the same in all of the tests, assuming of course that the component resistances do not vary to any great extent with the temperature. It follows that the temperature difference between the brick surface and the water is directly proportional

to the rate of heat flow from the one to the other. Considering the tests on the three other types of brick, with the exception of the Woodland test No. 3, the average rate of heat flow from the walls to the calorimeter was 1.32 g. cal. per sec. per sq. in., and the average temperature difference between the brick surfaces and the water in the calorimeter was 83° C. In the test on the magnesite brick the rate of heat flow from the wall to the calorimeter was 3.52 g. cal. per sec. per sq. in. (see below) while the average temperature of the water in the calorimeter was approximately 19° C. According to the above reasoning the temperature of the outer surface of the brick should have been

$$\frac{83 \text{ deg.} \times 3.52 \text{ cal.}}{1.32 \text{ cal.}} = 221° \text{ C.}$$

above that of the water, making the temperature of the surface $221 + 19 = 240°$ C. In Fig. 16 the calculated surface temperature is indicated by the point at the tip of the arrow.

Owing to the change in the direction of the temperature gradient the conductivity of the magnesite brick has been calculated for the range of temperature from 445° to 830° C., between which temperatures it is apparently constant.

Resuming the calculation, the rate of heat flow into the inner compartment of the calorimeter from 1 sq. in. of wall surface and through 1 sq. in. of the linoleum cover =

$$\frac{528 \text{ lb.} \times 454 \text{ g.} \times 5.47 \text{ deg.}}{1.5 \text{ hr.} \times 3600 \text{ sec.} \times 64 \text{ sq. in.}} = 3.79 \text{ g. cal. per sec. per sq. in.}$$

Rate of heat flow through linoleum cover: Temperature difference between air outside of calorimeter and water inside $= 40.0 - (22.5 - 2.7) = 20.2°$ C. Fig. 9 shows the rate of heat flow to be 0.27 g. cal. per sec. per sq. in.

Rate of heat flow from wall to calorimeter $= 3.79 - 0.27 =$ 3.52 g. cal. per sec. per sq. in.

Mean heat conductivity of the brick between 445° and 830° C.,

$$K = \frac{H\,x}{T_2 - T_1} \; \frac{3.52 \times 3.75}{830 - 445} =$$

0.0343 g. cal. per sec. per inch cube per C. degree.

The mean conductivities and resistivities of the materials tested are collected in Table V. Conductivities are expressed in gram calories per second per inch cube per degree C.; resistivities are expressed in thermal ohms per inch cube.

TABLE V.

Kind of Brick	Test No.	Mean Conductivity	Mean Resistivity	Temperature Ran
Woodland	1	0.00676	35.3	120° to 965° C.
Woodland	2	0.00666	35.8	100° to 1025° C.
Woodland	3	0.00704	33.9	400° to 995° C.
Quartzite	1	0.00679	35.2	100° to 935° C.
Quartzite	2	0.00670	35.6	100° to 960° C.
Star Silica	1	0.00794	30.1	100° to 910° C.
Magnesite	1	0.0343	6.96	445° to 830° C.

Aside from the above results, which indicate only the mean conductivities over the specified temperature ranges, the data secured in these experiments indicate the relationship between the conductivity of each of the materials and the temperature, and from them may be calculated the conductivity of each material at any given temperature and the mean conductivity over any range of temperature. These relationships are derived as follows:

When heat flows through a conductor bounded by two planes that are parallel to each other and perpendicular to the direction of heat flow, if H is the rate of heat flow expressed in gram calories per second through a section of the conductor having an area of A square inches, then

$$H = k \frac{A}{x} (T_2 - T_1)$$

wherein k is the mean conductivity of the material over the temperature range T_1 to T_2 in gram calories per second per inch cube per degree C.; x is the thickness of the conductor, *i. e.*, the distance in inches between the bounding planes; T_2 and T_1 are the temperatures C. of the hot side and cold side of the conductor, respectively. This equation holds not only for heat flow through the entire thickness of the conductor, but in the form

$$H = k A \frac{T_2 - T_1}{x_2 - x_1}$$

it is also applicable to the consideration of the heat flow between any two planes perpendicular to the direction of the flow and lying within the body of the conductor. In this case x_2 and x_1 are the respective distances of the two planes under consideration from a point of reference; in the following discussion the distances are measured from the cold surface of the conductor. T_2 and T_1 are the temperatures of the planes, and k is the mean conductivity of the material of the conductor over the temperature range from T_1 to T_2. Considering two planes that are close together, the ratio

$$\frac{T_2 - T_1}{x_2 - x_1}$$

expresses the slope of the temperature gradient between these planes, i. e., the temperature drop per unit of distance. The form of the equation just given shows that if the conductivity of the material changes with the temperature then the ratio

$$\frac{T_2 - T_1}{x_2 - x_1}$$

will also change, becoming smaller as the conductivity increases and larger as the conductivity decreases. In other words when heat flows at a uniform rate through a conductor bounded by two parallel planes that are perpendicular to the direction of heat flow, i. e., when the heat entering a unit area of the conductor on the hot side passes directly through to an equal area on the cold side without lateral loss and without being absorbed by the conductor, then the slope of the temperature gradient—the temperature-distance curve—decreases with increasing conductivity of the conducting material. The conditions of uniform heat flow, as thus defined, were practically realized in the case of the tests described above. Therefore the form of the temperature gradient determined during the course of each experiment furnishes the means whereby the relationship between the conductivity of the material and the temperature may be determined. It will be seen that all of the temperature gradients shown in Figures 10 to 15 possess the same general form; each is a smooth curve with its concave side toward the axis of abscissas, distances from the cold surface of the brick being plotted as ab-

scissas in all cases. The slope of each curve decreases with increasing temperature or with increasing distance into the brick, and this characteristic points to the generally known fact that the conductivity of such materials increases with the temperature.

In order to determine the actual relationship between the conductivity and the temperature the heat flow equation may be expressed in a slightly more convenient form, as follows: Imagine a plane passed through the brick of the test wall parallel to the hot and cold surfaces and perpendicular to the lines of heat flow. If H equals the amount of heat passing across A square inches of this plane in gram calories per second, then

$$H = A\ k\ \frac{dt}{dx},$$

in which k is the conductivity of the material at the temperature of that region of the wall through which the plane is passed; and $\frac{dt}{dx}$ is the slope of the temperature gradient at this point. From this equation,

$$k = \frac{H}{A} \Big/ \frac{dt}{dx}$$

in which the quantity $\frac{H}{A}$, the rate of heat flow through the wall in gram calories per second per square inch, is determined by the calorimeter during the conductivity test; while $\frac{dt}{dx}$ for any temperature may be estimated from the plotted curve of the temperature gradient, or, better, the equation of the plotted curve may be determined and its slope at any point may be obtained from the first derivative of the equation. The equations of the temperature gradients shown in Figures 10 to 15 have been determined, assuming that the curves are segments of parabolas with axes parallel to the axis of abscissas; on the plot of each curve the corresponding equation is given in two forms. The general form of equation for curves of this type may be written

$$t^2 + mt + nx + p = O.$$

In which t and x are the variables, temperature and distance, respectively, and m, n, and p are constants. The method of de-

termining the values of the constants that apply to the individual case consists simply of taking three sets of values for t and x, substituting these in the general equation, and solving the three simultaneous equations for m, n, and p. In each case the temperatures corresponding to the distances 0.5 inch, 2.0 inches, and 4.0 inches were substituted in the general equation.

It is evident that, with the constants of the temperature-distance equation known, the conductivity at any temperature may be calculated by substituting the value of $\frac{dt}{dx}$ for the given temperature together with the determined value of $\frac{H}{A}$ in the heat flow equation. The slope of the temperature gradient at any temperature is found by differentiating the equation of the curve and obtaining the first derivative. Differentiation of the general equation gives

$$2t\,dt + m\,dt + n\,dx = O.$$

The derivative is $\frac{dt}{dx} = \frac{-n}{2t + m} = \frac{-0.5\,n}{t + 0.5\,m}$.

Substituting this value for $\frac{dt}{dx}$ in the heat flow equation gives the general formula for the calculation of the conductivity at any temperature

$$k_t = \frac{H}{A} \cdot \frac{t + 0.5\,m}{-0.5\,n}$$

in which k_t is the conductivity at the temperature t. This method of interpreting the results makes the conductivity a lineal function of the temperature, and for convenience the conductivity of each material may be calculated at two temperatures; then by plotting these sets of conductivities against their corresponding temperatures on rectangular co-ordinates straight lines representing the conductivities of the materials at any temperature will be determined. Consider, for example, the conductivity of the Star Silica brick as determined by the experiment performed on it. The conductivity at 100 deg. C. is obtained by substituting in the foregoing equation the following quantities:

$\frac{H}{A} = 1.43$ g. cal. per sec., $t = 100°$ C., $0.5m = 880$, $-0.5n = 250{,}000$. Hence $k_{100} = 1.43 \cdot \frac{100 + 880}{250{,}000} = 0.00560$ g. cal. per sec. per cu. in. per degree C. Similarly $k_{1000} = 1.43 \cdot \frac{1000 + 880}{250{,}000} = 0.0108$ g. cal. per sec. per cu. in. per degree C. The fact that the temperature of the hot side of the wall during the experiment was only 910° C. does not invalidate the calculation of the conduc-

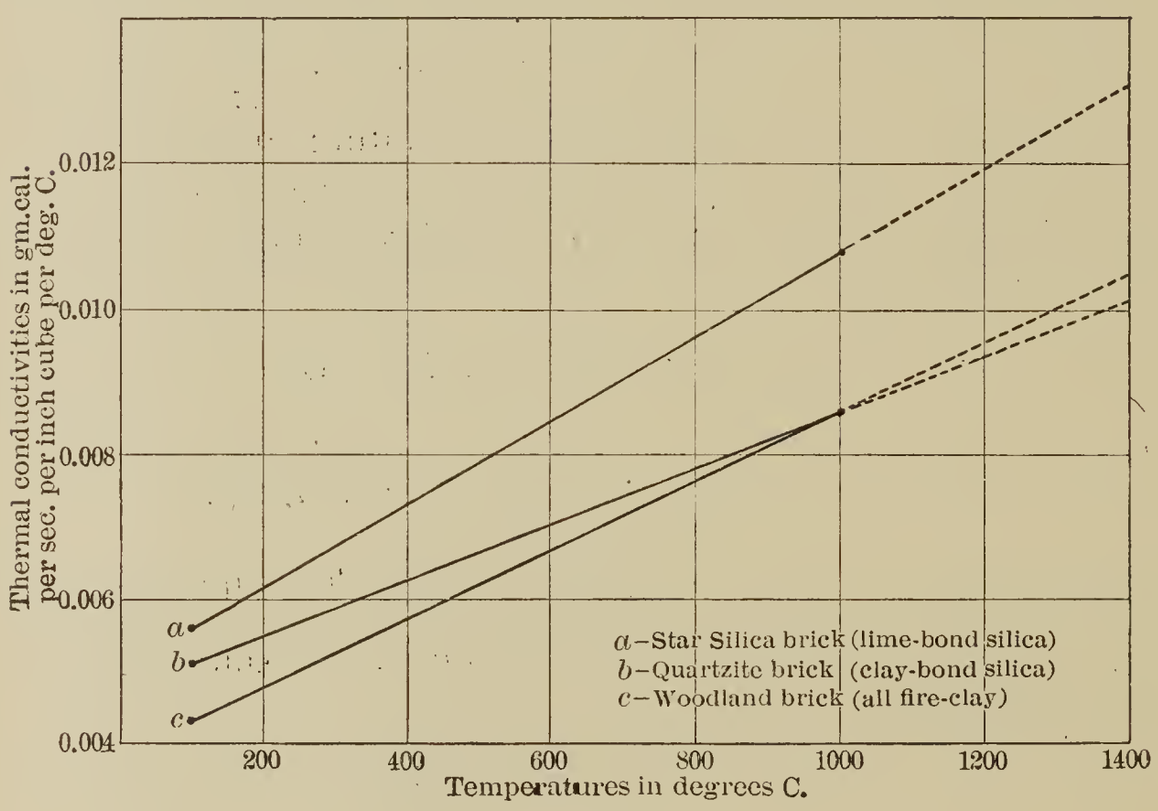

FIG. 17.

tivity of 1000°; such a calculation is simply extrapolation of the observed data, the temperature of 1000° being assumed for convenience. By this method the conductivity of the materials may be calculated for temperatures considerably higher than were attained experimentally; the conductivities thus calculated are, of course, open to question, but in the absence of actual measurements the figures thus provided will be of some use at least. It was stated above, by plotting on rectangular co-ordinates two calculated values for the conductivity of one of the materials against their corresponding temperatures a straight line is determined, each point of which represents the conductivity of

the material at a definite temperature. To obtain the mean conductivity over a range of temperature the conductivities at the extremes of the given range are averaged. By extending the line beyond the maximum experimental temperature the conductivities at higher temperatures may be estimated with some degree of accuracy.

This method of calculating the conductivities of the materials at various temperatures has been applied to the figures secured in each test, and the calculated conductivities at 100° and 1000° C. together with the mean conductivities over the experimental temperature ranges are shown in Table VI. Conductivities are expressed in gram calories per second per inch cube per degree C.

TABLE VI.

Material	Test No.	Exp. Temp. Range	Mean k Over Exp. Range	Calc. k at 100°	Calc. k at 1000°
Woodland	1	120 to 965	0.00676	0.00532	0.00816
Woodland	2	100 to 1025	0.00666	0.00438	0.00880
Woodland	3	400 to 995	0.00704	0.00332	0.00886
Quartzite	1	100 to 935	0.00679	0.00504	0.00880
Quartzite	2	100 to 960	0.00670	0.00521	0.00836
Star Silica	1	100 to 910	0.00794	0.00561	0.0108
Magnesite	1	445 to 830	0.0343	.....	0.0343

While the calculated conductivities are in some cases not in close agreement, in general they are consistent in indicating the relative conductivities of the various materials. Taking the averages of the figures applying to each material the conductivities at 100° and 1000° C. are given in Table VII.

TABLE VII.

Material	Average k at 100°	Average k at 1000°
Woodland	0.0043	0.0086
Quartzite	0.0051	0.0086
Star Silica	0.0056	0.0108

The reasons for not including the magnesite brick in the above table are outlined in the description of the test made upon that material. It was found that between 445° and 830° C. the conductivity of the magnesite brick was practically constant, the value being 0.0343 gram calories per second per inch cube per

degree C. Since further work on this material was not attempted, this is the only figure that can be offered. The figures given in Table VII have been plotted to scale in Fig. 17, in which the straight lines that join the plotted points have been extended to 1400° C.

Taking all factors into consideration, it is estimated that the precision of the figures representing mean conductivities is within 5 percent. The precision of the average figures representing the conductivities at definite temperatures is difficult to estimate, because these values not only depend upon the values assigned to the mean conductivities but also upon the accuracy with which the points on the temperature gradients were determined.

In conclusion it may be remarked that there are other methods that may be used in interpreting the data secured in this set of experiments, but the one that was adopted appears to be as rational as any. The figures thus provided, particularly those applying to the higher temperatures, will perhaps find use as a basis for conductivity calculations until by more and better work the conductivities of the commonly used refractories are actually measured over the higher ranges of temperature.

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DISCUSSION.

Carl Hering: Measurements of this kind are always welcome and of considerable value to those dealing with furnaces, because our knowledge of such conductivities, or resistivities as I prefer to call them, is very vague and uncertain.

There is no question that by the author's way of measuring the conductivity or resistivity he gets the true values for the material itself, separated and divorced entirely from another factor, namely the resistivity at the two surfaces, which may also be a very important factor. He has obtained what are doubtless very good figures for the conductivity of the material itself, perhaps the best on record so far.

In a furnace for which these figures would be used there is an additional surface resistivity which may at times be even more important than this resistivity of the material itself. In a metal coffee pot, for instance, this surface resistance constitutes virtually the entire heat insulation. In a steam boiler in which the heat travels from the flame to the water through the metal pipe, it was found a great many years ago that it did not make any practical difference whether copper or iron was used for the boiler tubes, because the heat resistance resided almost entirely at the surface. One can show this high surface resistance very nicely by pasting a postage stamp on the fire side of a boiler tube and it will be found to not even be charred; this shows that there is a very large heat gradient in the few thousandths of an inch on the surface of these tubes. Hence, the figures which Mr. Dudley gives, while of interest and of value, do not include all the figures which we need in designing furnaces; those representing the surface resistance are still wanting. Mr. Dudley has eliminated something in his calculations which other observers have not been so careful to eliminate, namely the heat insulating effect of joints. He has made his wall one brick thick, thereby avoiding the joints. In many other published tests the wall was sometimes made of two or three bricks thickness, in which case the resistivity of the joint was included, and this may be so great, in comparison to the other, as to seriously mask results.

In general, such a method of measuring as that used by this author involves a rather large error, because the temperature rise of the water is not great and when there is such a small rise the temperature must be read very precisely to give accurate results. I have seen experiments in which this rise of temperature was represented by not more than one-eighth or three-sixteenths of an inch on the scale, hence an error of only 1-32 inch (0.8 mm.) in the reading would be a very large percentage error in the temperature.

It should be noted that Mr. Dudley gets his final temperatures by extrapolation, not by measurement. He plots his curve for temperatures and then extends it to the outside surface, hence gets the outside temperature of the surface by extrapolation alone, which is sometimes a dangerous thing to do.

Another feature which may be criticized is that he paints both surfaces with Portland cement, therefore he does not get the true surface conductivity of the fire-bricks; the surface conductivity which he gets may be different from that of the brick. But this does not matter in his test, because he measured only the conductivity of the material itself, and divorced it entirely from the surface conductivity.

The paper unfortunately is extremely long. It seems to me that if it had been cut down to one-half or one-quarter of its present length, it would have been still more interesting.

Frank Thornton, Jr. (*Communicated, read by C. G. Schluederberg*): There is a great deal of merit in the paper under discussion, as it describes a method of determining heat conductivity along lines somewhat different from those usually followed. We will all agree that there is great need for more reliable information as to the exact thermal conductivities of the heat insulating materials, and that improvement in thermal insulation is highly desirable. That is especially true when electricity is the source of heat.

The author has made careful and painstaking efforts to avoid errors in measurement, but it seems to the writer that there is a great source of possible error in the construction of the calorimeter itself. That such an error may exist is shown by the fact that the author's results average higher than those obtained by other investigators of the same class of materials. For a test wall four and one-half inches (11.5 cm.) thick, he has chosen to measure the heat arriving at the surface over an area 8 x 8 in. (20 x 20 cm.), and for protection and insurance of uniform and parallel flow of heat perpendicular to the surface he has used a guard ring only two inches (5 cm.) wide. That means that the width of the guard ring is less than one-half the thickness of the wall of the material being measured. Since the surface of the wall outside the calorimeter would be at a higher temperature than that under the calorimeter, there would be a flow of heat from that portion of the wall toward the calorimeter. It is very doubtful whether such a narrow guard ring can be relied upon to absorb it all, or to prevent a distortion of the flow of heat from parallel paths. This ring should certainly have

been made at least 9 inches (22.5 cm.) wide, and preferably greater.

An electric heater would have been much more convenient than the coke fire used and would have made it possible to have obtained a more uniform distribution of the heat over the hot surface of the wall.

The variation of the thermal conductivity with the temperature is often overlooked, but the author has brought it out quite clearly. For this reason great care must be exercised in using average values.

Mr. Dudley should be commended for the thoroughness with which he has performed these tests and the completeness of his report.

H. K. Hitchcock: I have been very much interested in the paper which Secretary Richards has abstracted, and I think it is one of the subjects in which engineers generally are interested. In regard to Dr. Hering laying so much emphasis upon the surface resistance, he has forgotten that a furnace wall is not the shell of a boiler, and that the primary function of the furnace is to keep the heat in the furnace, and not to transmit it. In selecting material for the design of a furnace, the first thing the engineer wants to know is its thermal conductivity or resistivity. The next things desired are the way it behaves under the influence of heat, the amount of pressure it will stand structurally under the heat treatment, and the way it will behave when alternately heated and cooled, whether it will disintegrate or spall off or whether it will not, under these conditions.

I do not think that the method employed here could be greatly improved upon, nor the general character of the curves submitted. They verify data obtained by me in two very elaborate series of experiments made many years ago.

As regards the protecting ring around the calorimeter, my own judgment is that the depth and size of the ring are ample to insure accurate work, and any errors, even if present, would be negligible.

Carl Hering: Mr. Hitchcock has misunderstood me. I of course know the difference between a boiler and a furnace; the function of a boiler is to transmit heat, while that of a furnace

wall is to keep it from being transmitted. I simply cited the boiler as an extreme, well known and striking case, in which that surface resistance is exceptionally great. I do not agree with Mr. Hitchcock that the surface conductivity can be neglected in the case of furnaces, though of course it will be much smaller than in boilers. Some of you may recall that Secretary Richards and I had quite a long discussion of this subject in a technical journal. In my opinion, this surface resistance may be a very important element, and one which I hope will receive attention from some one who can make as careful and accurate experiments as Dr. Dudley did in measuring the internal conductivity of the material itself. I do not wish to reflect in the least on his experiments; on the contrary, I am inclined to believe that his results for the solid material are probably very reliable, perhaps the best so far on record; but those who build the furnace need the other figure too, because it may be quite great. Foundrymen tell us that by merely whitewashing the outside of furnaces the heat from them is much less oppressive; this shows that the surface resistance must have been quite low, if a mere change of the surface makes so great a difference. It is also well known that a polished coffee pot will keep the coffee hotter than one that is dull. Dr. Langmuir has shown us in a recent paper that silver plating a surface increases its surface resistance.

H. K. Hitchcock: As a matter of fact, I know a little something about this, and think that the contrary is the case. For instance, if I were to plot curves for a 4.5 inch brick wall, the ordinates representing the degrees of temperature and the abscissæ representing the B. T. U.'s passing through that wall, the character of the curves would look very much like those shown in Fig. A. Curve (1) would be the temperature of the gases under the crown or against the side wall of the furnace. Curve (2) would be the temperature of the inside surface of the arch or wall, and curve (3) would be the temperature of the outside surface of the wall. Now, at any particular point here, as at X, the lengths of these vertical lines A, B and C cutting these curves, represent the resistances of the various elements to which Dr. Hering has referred. A equals the resistance capacity of the outside surface of the wall. B represents the resistance to flow

through the wall, and the little line (C) represents the resistance of the surface on the inside of the wall. Now, on the other hand, if we have a nine inch (23 cm.) wall, or crown, and we will use the same temperature for the outside of the wall,

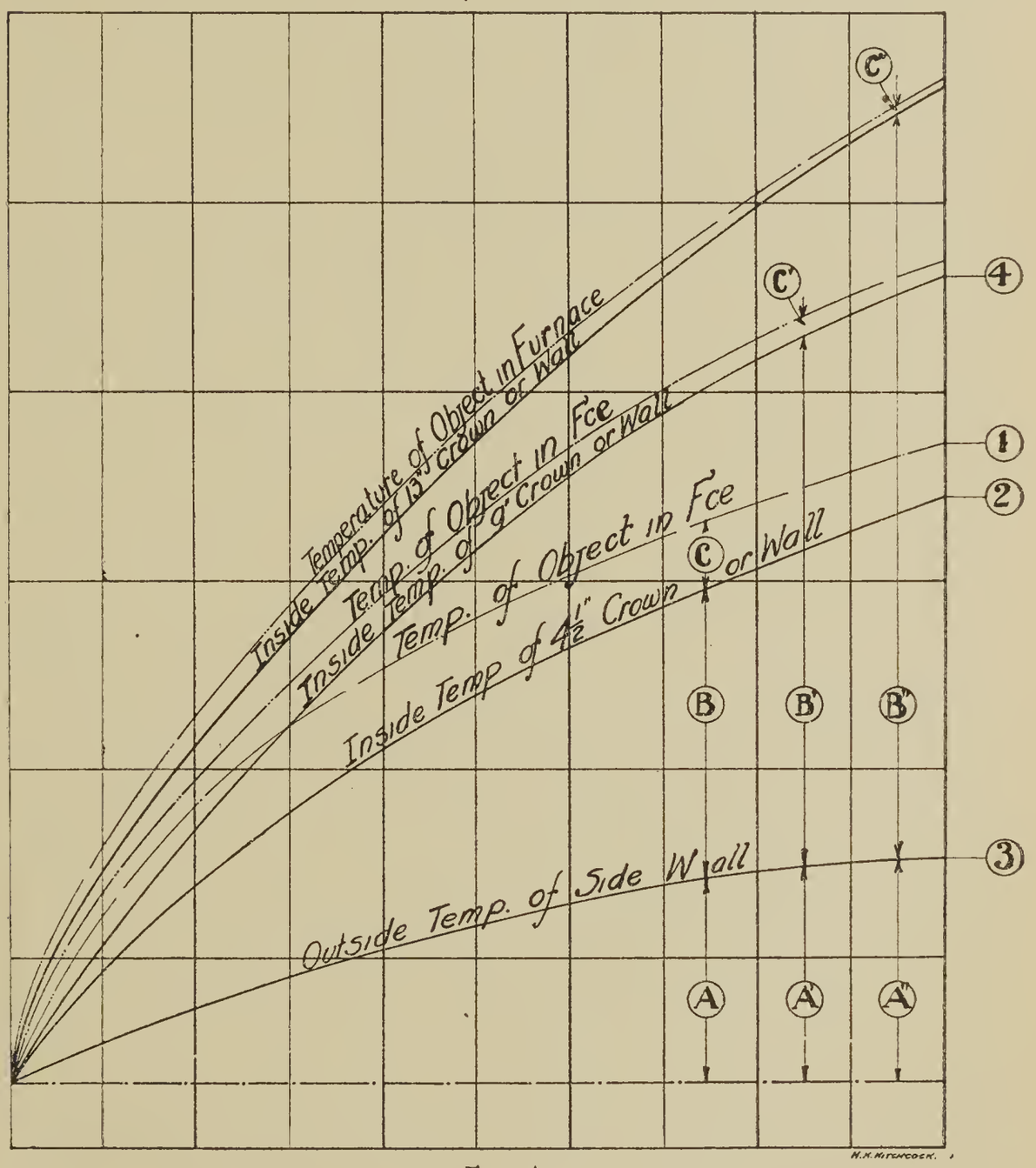

Fig. A.

this curve (4) will go higher up somewhere here, and if it is a 13 inch (33 cm.) wall it will go still higher up and with the same temperature of the furnace, the heat dissipated will be reduced accordingly while the surface resistance will remain the same in each case. Increasing the resistivity of the wall is

equivalent to increasing the thickness, and is what we are all aiming at.

CARL HERING: The surface resistivity may often be far greater than that shown in Mr. Hitchcock's diagram. I fear he greatly underestimates its importance, at least in some cases.

H. C. CHAPIN: It seems to me that Mr. Dudley's data serve very well so far as they go, and that they could be made to serve Dr. Hering's requirements simply by addition of supplementary data on surface conductivity.

CARL HERING: Mr. Dudley does not give the true flame temperature in the inside; he merely extrapolates the temperature of the hot side of the wall and gets 900°. We know that the coke fire must have been considerably over 900°. The drop of temperature between the flame and the inside surface must have been several hundred degrees, in a space of probably a few thousandths of an inch, showing an extremely high surface resistance. There is a second surface resistance on the outside, though this is probably much less.

H. C. CHAPIN: I believe that I can make my contention clearer through the more familiar analogy of an electrical conductor, for example, a carbon electrode, the conductivity of which we measure by voltage drop for a given electrical current just as Mr. Dudley measures thermal conductivity by temperature gradient for a given thermal current. In one case we have a contact resistance between source of electrical current and carbon, in the other a contact resistance between flame and brick, but in neither instance does this affect the results for the conductivity of the material in question. It is quite true, as Dr. Hering states, that data on the thermal conductivity of a brick unsupplemented by data on temperature gradient between brick and source of heat does not represent the complete insulating value of the brick; but it represents the only factor in this value which is wholly characteristic of the brick itself. Once determined, this can be applied to numerous observations of total insulating value for calculation and classification of thermal contact resistances, which vary greatly with nature of surface and source of heat.

E. F. NORTHRUP: I wish to make a few remarks in favor

of a high type of altruist. I refer to the man who goes into the laboratory and makes careful, painstaking measurements. The data which he gathers and the measurements which he makes, if they have any value at all, are of value chiefly to others rather than to himself. He seldom receives any money for his work, and as the data are of chief value to others, he is certainly an altruist. The author of this paper evidently has spent a great deal of time in taking a large number of observations.

I have not analyzed the paper under discussion with sufficient care to know if the data collected are praiseworthy or not, but judging from the discussion of the paper it seems to me that they are. Heat measurements are the most difficult kind of measurements which are made in the laboratory. The movement of heat is so extremely slow that very tedious, painstaking work has to be done in order to get measurements which are at all accurate. One must wait for temperature equilibrium and if one has patience to carry through a series of heat measurements and get anything at all which is an advance on previous knowledge, he deserves the commendation and thanks of engineers.

Francis C. Frary: It seems to me that probably the difference of opinion between Mr. Hitchcock and Mr. Hering is due to the difference in the relative resistance of what they had behind their surface film. It is like putting a resistance of one ohm in series with a resistance of one-hundredth of an ohm, and saying that the one ohm is practically the whole thing, then putting one ohm in series with one hundred ohms, and still considering that the one ohm is the important thing.

Jos. W. Richards: Mr. Dudley's results would be more useful to engineers if he expressed the conductivities of the materials as a constant, at 0° C., plus a function of the temperature, such that $K_t = \alpha + 2\beta_t$. Outside of magnesite, all Mr. Dudley's results can be thus expressed, meaning simply that the conductivities are straight lines increasing with the temperature. A simple derivation from this gives the mean conductivity from 0° C. to t° as

$$K_m = \alpha + \beta_t.$$

while the mean conductivity between any two temperatures, t′ and t″, is

$$K_m = \alpha + \beta (t' + t'')$$

I have calculated these expressions for the materials tested, and find the constant to be:

	α			β		
	Cal. per inch cube	Cal. per cm. cube	Reciprocal thermal ohms	Cal. per inch cube	Cal. per cm. cube	Reciprocal thermal ohms.
Woodland Brick	0.0038	0.0015	0.0040	0.0000024	0.0000010	0.0000025
Quartzite "	0.0047	0.0019	0.0049	0.00000195	0.0000008	0.00000205
Star Silica "	0.0050	0.0020	0.0052	0.0000029	0.0000016	0.0000030

I further believe that results should always be expressed in all such papers in calories/deg/sec/ cm. cube and also in reciprocal thermal ohms.

Boyd Dudley, Jr. (*Communicated*): The question of surface resistance to the flow of heat seems to have been the point about which much of the discussion of my paper centered. My failure to make a study of this factor was not due to a lack of interest in it nor to a lack of appreciation of its importance, but rather to a lack of the knowledge as to just how such a study could be properly made.

Contact or surface resistances to heat flow are very difficult to study and correlate, because of the exceedingly great influence of changing conditions upon them. For example, the resistance of the surface of contact between a solid and a gas depends to a great extent upon the rate of motion of the gas. While a knowledge of such resistances is extremely useful and frequently necessary, I believe with Mr. Hitchcock that in most cases of furnace construction such resistances are of secondary importance. Let it be expressly understood, however, that I am advancing no arguments against whitewashing the outside of a foundryman's furnace or polishing the outside of a coffee pot. Such practices, without doubt, are good; they serve to restrain heat flow across the respective surfaces. Furthermore, the whitewashed furnace (so long as it remains white) improves the

appearance of the foundry, and the burnished coffee pot lends an air of distinction to the breakfast table. But, as measures in the interest of heat conservation, I believe it will not be denied that an extra course of brick on the furnace and a flannel jacket on the coffee pot would be more effective.

It appears to me that in the extensive work of Dr. Langmuir,[1] on the radiation and convection of heat from surfaces, we already have a fund of information that may be applied to problems of heat flow across gas-to-solid contacts. The only factor that is needed in applying his data directly in cases involving smooth brick walls is the emissitivity of the brick, and by making reasonable assumptions in regard to this point we have information available that should be of great use to those who are particularly interested in this phase of the subject.

In regard to the width of the guard ring of the calorimeter, referred to by Mr. Thornton, this point was made the subject of a fairly thorough preliminary investigation and numerous calculations, and two inches (5 cm.) was determined upon as a safe figure for the width of the guard around the inner compartment. As evidence supporting the view that this width is sufficient, I wish to call attention to the fact that in each test three sets of temperature measurements were made through the test-wall. One pyrometer hole was in the wall at the center of the inner compartment of the calorimeter. A second hole was at the left-hand edge of this compartment and near the upper edge, while the third hole was on the right-hand edge and near lower edge. Had there been a lateral influx of heat to that portion of the wall covered by the inner compartment of the calorimeter, then the temperature gradients obtained by measurements in the marginal holes would have differed from that obtained by measurements in the center hole in such a manner as to make this influx apparent. An examination of the records of the tests will show that no such differences existed between the temperature gradients of the outside holes and that of the inside hole.

[1] Trans. Amer. Electrochem. Soc. 23, 299. (1913),

A paper presented at a joint meeting of the American Institute of Electrical Engineers and the New York Section of the American Electrochemical Society, March 12, and called up for discussion at the Twenty-seventh General Meeting of the American Electrochemical Society at Atlantic City, April 23, 1915, President F. A. Lidbury in the Chair.

FIXATION OF ATMOSPHERIC NITROGEN.

By Leland L. Summers.

Abstract of Paper.

The nitrogen contained in the atmosphere is in an inert form and does not readily lend itself to chemical reactions. To overcome this is the province of "nitrogen fixation."

There are very definite commercial limitations involved in accomplishing this as the world's supply of nitrogen has been readily obtained from vast natural deposits of sodium nitrate in Peru and Chile and the production of a substitute must be at a competitive cost.

The electrical processes for fixing nitrogen have a very low efficiency, due to utilizing thermal energy only.

Combinations of electrical and chemical methods promise the most important developments.

Comparative figures are given showing amount of energy necessary per kilogram of nitrogen fixed, and the general economics of the subject are discussed.

Introductory

In 1898 Sir William Crookes in his address as President of the British Association very forcibly pointed out that the commercial fixation of atmospheric nitrogen was one of the greatest discoveries awaiting the ingenuity of chemists. He emphasized with very interesting figures its important practical bearing on the future welfare and happiness of the civilized races. This address brought forcibly to the attention of engineers the fact that the existing sources of fixed nitrogen were limited, and greatly stimulated the efforts of investigators. The problem itself had been worked on for over a century, as it was known that nature fixed nitrogen of the atmosphere by means of electric discharges, and Cavendish in 1781 had shown that a small amount of nitrogen was converted into nitric acid in the combustion of hydrogen with oxygen to form water, while Bunsen in 1877 obtained favorable yields by means of gaseous explosions. The earlier efforts commercially in the art were, however, largely confined to the fixation of nitrogen for the

purpose of manufacturing cyanides, and the earlier bibliography of the subject therefore deals almost entirely with these efforts.

Commercial Products of Nitrogen. The three fundamental commercial products formed by nitrogen are: first, its union with oxygen to form nitrates, XNO_3, and nitrites, XNO_2; second, its union with carbon to form cyanogen C_2N_2 and producing cyanides XCN and cyanamids XCN_2; third, its union with hydrogen to form ammonia, NH_3. From all of the above products there are obtained a large number of derivatives used in the chemical arts.

The most important of all commercial products are the unions of nitrogen with oxygen, forming the nitric acid salts of commerce. These are of particular importance on account of the vast natural deposits of nitrate of sodium occurring in Peru and Chile, commonly called Chile saltpeter. Practically, this commodity is the one that sets the price for all other compounds of nitrogen, as it has been mined in Chile since 1830, and during the past twenty-five years its production has assumed vast proportions, the present annual output amounting to about 2,500,000 tons. This deposit of Chile appeared inexhaustible, and therefore there was no occasion for alarm regarding the world's supply of combined nitrogen; but after years spent in exploration work it began to appear that the Chilean deposits would be exhausted before the end of the present century, and since then all other sources of combined nitrogen have received attention.

While there are a few scattered natural deposits other than those in Chile, there is none which has at the present time a chance of competing, most of them being of limited extent and situated in inaccessible regions. In Chile the deposits are easily worked, and even after years of careless mining, with no effort to effect economies, the present cost of producing nitrate is not excessive, varying from $10 to $20 per ton and selling in Liverpool for about $45 per ton. This leaves a profit of from $5 to $10 a ton on the operation, after paying the Government of Chile an export tax of about $12.25 per ton. In the past thirty years this export tax has netted the Chilean Government about $500,000,000. Of the total production of Chile the United States imports about 600,000 to 700,000 tons per annum, the

balance being practically all shipped to European countries. Chile saltpeter has sold as high as $60 a ton, but since 1909, when the agreement among the producers expired, the price has approximated $45 per ton f.o.b. Liverpool, making a price of from $35 to $40 per ton f.o.b. Chile.

The union of nitrogen and carbon to form cyanides and with hydrogen to form ammonia are two of the earliest forms in which the combined nitrogen was utilized. Most all animal and vegetable refuse contains ammonia compounds, and these were the early sources of ammonia, and animal refuse products such as hides, hoofs and horns were the sources of combined carbon products forming the cyanides. Until the discovery of the McArthur-Forrest process for gold extraction, the markets for cyanides were comparatively limited and there was no great effort made to produce them on a large scale. With the rapid development of this art in the recovery of the low-grade gold deposits, a sudden impetus was given to the cyanide industry, and large quantities of cyanides are now manufactured from ammonia and metallic sodium. Small amounts of cyanides for industrial purposes are recovered from the gas retort houses, but these processes are not generally applied, and no particular effort has been made to extend the processes to the recovery of cyanides from by-product coke ovens. The greater portion of the cyanides are manufactured in England and Germany, and some 20,000 tons per annum are exported annually by these two countries. As the cyanides of sodium and potassium for gold recovery purposes sell from $300 to $400 per ton, they represent one of the highest prices of nitrogen directly combined with a simple element.

The third great commodity of commerce, ammonia, is utilized extensively in industrial arts, but, in addition, has been used for many years as a fertilizer. The annual production of sulphate of ammonia now amounts to about 1,250,000 tons, and the Liverpool price approximates that of sodium nitrate, varying from $45 to $60 per ton. Practically all of this sulphate of ammonia is manufactured from coal distillation either from gas-house retorts or by-product coke ovens, up to the past year there having been practically no process in operation for the direct synthesis of ammonia from its compounds.

All the older retort processes for the manufacture of gas recover ammonia by washing the illuminating gas with water. All by-product coke ovens likewise treat the by-product gas for the recovery of ammonia. American coals run from 0.9 percent to 1.4 percent nitrogen, or from 18 to 28 lb. (8.1 to 12.7 kg.) of nitrogen per ton of coal. In the distillation of this coal, about 20 percent of the nitrogen is recovered from the gases of distillation, so that from 4½ to 7 lb. (2.1 to 3.2 kg.) of ammonia are recovered per ton of coal distilled; this ammonia when united with sulphuric acid forms sulphate of ammonia, giving a yield of from 18 to 28 lb. (8.1 to 12.7 kg.) of sulphate of ammonia per ton of coal distilled. Weak solutions of ammonia water are concentrated from the gas-house retorts and the ammonia distilled from this water by breaking down the ammonia contents with lime, the pure ammonia being then united with sulphuric acid. In many of the coke oven plants the sulphate is formed directly by passing the gases into sulphuric acid, forming the ammonia sulphate by a direct process.

In general it costs about $15 per ton of ammonia sulphate to manufacture the sulphate from the ammonia, so that if ammonia sulphate is selling for $45 per ton, $15 of this is represented in the cost of sulphuric acid and the manufacturing, making the net ammonia cost, with profit, $30 per ton of sulphate or, as the nitrogen content of the sulphate amounts to 21 percent, the nitrogen represents an actual value of 7 cents per pound. With the great increase in the number of by-product coke ovens, there has been a greatly increased quantity of ammonia sulphate manufactured, and it would seem that under these conditions the price of ammonia sulphate will tend to diminish rather than to increase. The actual cost to the by-product coke oven plants recovering the ammonia, in addition to the $15 for manufacturing the sulphate of ammonia, will approximate $10 per ton, and if there is any profit to be obtained from the sale of ammonia, they can afford to recover it at this figure.

Another source of ammonia by coal distillation is from producer gas generated on what is known as the Mond system. In this process steam is admitted to the producer in excess, so that the temperature is not permitted to rise to a point where the ammonia liberated by the fuel is decomposed. This excess of

steam tends to protect the ammonia, and it is recovered from the producer gas by washing. In this process not only the ammonia carried in the volatile products is recovered, but also a large percentage which ordinarily remains in the carbonaceous residue of the coke oven and gas-house retort. As ordinarily distilled, about 50 percent of the total ammonia of the coal remains in the coke residue and is not recovered. In the producer, where this coke is consumed in the presence of steam, the total percentage of recovery may be as high as 75 percent of the theoretical nitrogen contained in the coal, so that from 15 to 20 lb. (6.8 to 9.1 kg.) of nitrogen may be recovered, or, in terms of ammonia sulphate, from 60 to 80 lb. (27.2 to 36.2 kg.) of ammonia sulphate may be obtained per ton of coal consumed in the producer. This type of producer has not been extensively utilized in America, as the expense of installation is increased by the necessity of washing a very large volume of low-grade gas, the volume of gas per ton of coal consumed in the producer being about 130,000 cu. ft. against about 10,000 cu. ft. per ton of coal, as distilled in the coke oven.

A number of these plants have been installed in England and on the continent, but the aggregate of the ammonia sulphate produced is not large as compared to that from coke ovens and gas house retorts.

Available Nitrogen in Commercial Products. The question of the available nitrogen in the various compounds has, in a measure, determined the price of the product, the utilization in the fertilizer art being practically the basis of fixing the price. For a number of years it has been assumed that the selling price of combined nitrogen would be from 12 cents to 13 cents a pound. Thus Chile saltpeter being about 95 percent pure, nitrate of soda would have a theoretical nitrogen content of about 16.5 percent or, corrected for impurities, would have about 15.5 percent nitrogen.

As the cyanides, until recently, were not used directly in the fertilizer art, and were combined with more expensive products, their price has not been regulated by their content of combined nitrogen. The ammonia used in the fertilizer art is almost entirely used as sulphate of ammonia, on account of the cheapness of the commercial sulphuric acid and the ease of manu-

facture, and this product would therefore have a theoretical content if 21 percent of nitrogen.

The above nitrogen products may be considered the fundamental commercial forms in which combined nitrogen enters the market, and while the fertilizer industry fixes the price of combined nitrogen, it is only one of the many industries in which vast quantities of nitrogen are utilized. Thus about 50 percent of all the Chile saltpeter imported in this country is used in the manufacture of explosives, while an additional 25 percent is utilized in the arts requiring nitric acid. Of the ammonia sulphate, a very large percentage is used directly as fertilizer, though there is a very considerable demand for use in chemical industries and such commercial applications as anhydrous and aqueous ammonia used in the refrigeration art. Practically all explosives have utilized nitrogen compounds as a principal ingredient. The earlier makers of black gunpowder used Chile saltpeter, charcoal and sulphur and the later so-called smokeless powder utilizes the oxygen-carrying property of nitrogen as well as the inherent molecular energy in the production of such high explosives as nitroglycerin, cordite, lydite, mellenite, gun cotton and various other nitro-cellulose compounds, and modified explosives used in industrial work, such as dynamite and various blasting powders.

Fixation Processes. In considering the fixation of atmospheric nitrogen from a commercial standpoint, the limitations will be imposed by the selling price of the natural product from Chile, covering nitrate compounds, and the selling price of ammonia sulphate, as obtained from coal distillation, affected as these prices will be by the manufacture of ammonia from atmospheric nitrogen.

In competition with the above sources of nitrogen there has been the constant effort toward the fixation or rather the utilization of some of the vast quantity of atmospheric nitrogen surrounding us.

A list of these fixation processes would contain the names of hundreds of investigators, and from the past twenty years of effort there may develop processes which at present are still experimental; but of the various processes which have reached

the state of commercial application there appear to be four distinct lines of development.

First. The production of nitric acid directly from the atmosphere by means of the electric arc. In this process the nitrogen of the atmosphere is directly combined with its accompanying oxygen without utilizing any other chemical substances, the process consisting essentially of a powerful arc furnace through which air is forced, causing at this high temperature the nitrogen to combine with the oxygen, forming nitric oxide, NO.

Second. Methods of fixing nitrogen by means of electric furnaces or combustion where the energy of chemical combination is utilized, causing the nitrogen to combine with some substance with which there is a pronounced energy of chemical combination. These processes include furnaces utilizing calcium carbide, with which nitrogen readily combines to form calcium cyanamid, $CaCN_2$, and various processes for making combinations of nitrogen and a basic or alkaline earth metal such as calcium nitride, Ca_3N_2, or magnesium nitride, Mg_3N_2, or aluminum nitride, AlN, the chemical action usually forming a nitride or carbonitride.

Third. Processes for producing ammonia, NH_3, directly from nitrogen and hydrogen. These include the effort to use the various forms of electric discharge by which the nitrogen molecule may be decomposed and, in the presence of hydrogen, form ammonia. As ammonia decomposes at a very low temperature (500 to 1,000 deg. cent.), only the silent discharge seems available, and the yields are not commercial. The most promising of all direct ammonia processes seems to be that of Haber. In this process a catalytic agent is used, and under a heavy pressure the nitrogen molecule is decomposed and united to the hydrogen, thus forming ammonia. Salts of uranium seem to be preferred as the catalytic agent, and have the power of acting on nitrogen at a temperature of about 500 deg. cent.

Fourth. Production of a high temperature by combustion, utilizing either catalytic agents or simply by producing a high temperature by means of the explosion or combustion of gases directly combining the nitrogen and oxygen to form nitric oxide, NO. This method, early used by Bunsen in the combustion of

hydrogen to form water, has been applied to coke oven gases by Hausser. A bomb is used and the mixture of gas and air is fired electrically, the small amount of NO formed is recovered and converted into nitric acid, HNO_3.

The chemical form in which the commercial supplies of combined nitrogen appear on the market is due largely to existing commercial conditions. The nitric acid combined as sodium nitrate occurs in this form simply on account of being naturally produced in this form. The ammonia appears on the market as ammonia sulphate largely on account of the cheapness with which sulphuric acid can be obtained, and the widely distributed plants for its manufacture, making it one of the cheapest and most convenient forms of combining with ammonia. It is probable that in commercial nitrogen fixing plants, if both ammonia and nitric acid are manufactured, one of the most convenient forms for marketing this product will be by using nitric acid in place of sulphuric acid, making ammonia nitrate, NO_3NH_4. This product is on the market at present, but is only manufactured from sodium nitrate and from ammonia, or in some of the plants where nitric acid is manufactured, ammonia is shipped to the nitric acid plants to be manufactured into ammonia nitrate. The advantage of ammonia nitrate is that it has a nitrogen content of 35 percent in this respect, being a much more concentrated nitrogen product either for the processes of manufacturing other compounds of nitrogen or for use in the fertilizer industry.

Physical Limitations and Those Fixed by Natural Sources. The competition with natural sources will fix the commercial limitations or selling prices for these various nitrogen compounds and in considering the possible developments of the processes it will be interesting to see to what extent they have definite theoretical limitations, as these will greatly affect any comparison of possibilities. Before considering in detail these processes we might endeavor to investigate whether our present conception of the physical and chemical reactions involved impose real limitations, or whether there is an uncertain boundary which further developments may encroach upon, perhaps thus continually improving the efficiency and possibilities commercially. If, for instance, the nitric oxide processes which utilize only 2 percent to 4 percent of the energy supplied to the furnace are limited

to this amount by the inefficiency of the apparatus, there is much greater possibilities of development than would be the case if the process has definite physical or thermodynamic limitations, and the present apparatus utilizes a favorable percentage of this possible ultimate limit. To some extent these theoretical limitations are not always sharply defined, and research will extend this horizon, but we may determine some of these limitations quite definitely.

II. Theoretical Limitations

As we are considering this subject from its engineering aspects, it may be excusable to examine some of the theoretical limitations imposed by the laws of physical chemistry, and in reviewing what may be termed elementary formula, it is interesting to note that the investigation of these theoretical limitations has been of fundamental importance to physical chemistry in extending the application of the laws of chemical dynamics.

Molecular Inertness of Nitrogen. The elements carbon, C, and nitrogen, N, possess a marked similarity in the fact that the molecule of each is composed of two or more atoms united together with a bond representing a large amount of energy. Nitrogen, having an atomic weight of 14, has a normal molecular weight of 28, indicating two atoms to the molecule, and in this molecular form it occupies 79.2 percent of the volume of the earth's atmosphere. To separate this molecule into its constituent atoms and cause these atoms to combine with other elements is the problem of the fixation of nitrogen. Unless combined in the atomic form, the enormous bond between the atoms causes them to combine upon themselves into the inert form of molecular or atmospheric nitrogen. The ordinary compounds of nitrogen are formed only by expenditure of a large amount of energy, the union of molecular nitrogen, N_2, and molecular oxygen, O_2, to form nitric oxide, NO, being represented by the formula,

$$N_2 + O_2 = 2NO = -43{,}000 \text{ calories}$$

Or in other words, to form one gram molecule of nitric oxide, NO, requires the expenditure of energy amounting to 21,500 calories.

The general similarity to carbon in this molecular inertness makes an interesting comparison.

Thus

$$C_2 + O_2 = 2CO = 58{,}000 \text{ calories}$$
$$2CO + O_2 = 2CO_2 = 134{,}000 \text{ calories}$$

The formation of one gram molecule of CO therefore represents the liberation of 29,000 calories, while the formation of one gram molecule of CO_2 from CO represents 67,000 calories or a total of 96,000 calories in the formation of CO_2 from the original elements C and O. When amorphous carbon therefore is caused to assume the gaseous condition and unite with a molecule of oxygen, there is liberated 29,000 calories, but after assuming this condition in which the molecule is no longer composed of the inert carbon molecule, a second gram molecule of oxygen unites with the CO and liberates 67,000 calories additional. The second molecule of oxygen therefore liberates 38,000 calories more than the first molecule, and as the oxygen molecules were alike, this energy represents the bond uniting the carbon atoms and the energy necessary to break down the bond between these atoms and produce a gaseous condition from the amorphous condition.

Returning to the nitrogen molecule, it is apparent that the formation of the gram molecule of NO requires 21,500 calories in comparison to carbon liberating 29,000 calories to form CO; that is, the nitric oxide reaction is endothermic while the carbon monoxide reaction is exothermic. Upon adding a second molecule of oxygen to the nitric oxide to form the peroxide, we find,

$$2NO + O_2 = 2NO_2 = 27{,}000 \text{ calories}$$

or 13,500 calories per gram molecule are liberated after previously expending 21,500 calories to form NO. Since there is liberated only 13,500 calories upon adding a second molecule of oxygen, the net energy required to form NO_2 would be 8,000 calories. The first molecule of oxygen required 21,500 calories, whereas the second required only 8,000 calories, so that 13,500 calories were required by the nitrogen molecule to prepare it for combination with the oxygen.

Dynamic Equilibrium. These heats of combination developed by the atoms combining upon themselves indicate a very stable

or inert molecule, and in liberating this energy to assume this more stable form, the forces exerted are of large magnitude. It is readily apparent from this, for instance, how carbonaceous gases can readily form soot and cinders and other amorphous forms, when the union with oxygen is disturbed, as the tendency of the atoms to unite with oxygen or to form carbon molecules will depend upon an adjustment of the surrounding conditions. This ever-changing condition of equilibrium constitutes the dynamic conception of equilibrium displacing the static equilibrium of the older theories of chemistry. In order to more carefully consider some of the theories that have been advanced, it may be of interest to follow further some of the concepts of physical chemistry. The fact that the nitrogen atom has this strong tendency to combine upon itself with a liberation of energy greater than the combination with the oxygen atom, indicates that in any reaction, when the combination with oxygen has made possible a changing of the atoms, there will be continuously in progress an action and a reaction and the equilibrium will be indicated by the expression

$$N_2 + O_2 \leftrightarrows 2NO$$

the sign of equality being displaced by the two arrows indicating that the action proceeds in each direction; that is, it is a reversible reaction, and the equilibrium will be dependent upon conditions, the two most important conditions being temperature and the active masses of the substances present. Considering first the effect of the active masses present, if it be assumed that the collision of molecules causes the re-arrangement of the atoms comprising the molecule, and that of these collisions only a certain number will cause the re-arrangement to proceed in one direction, the re-arrangement will be greater the more frequently the collisions take place, there being some ratio for each individual case, and the collisions possible will obviously be proportional to the concentration present; that is, the collisions will be proportional to the number of molecules present. With two substances present, the collisions will be proportional to the molecules of each present and hence to their product.

The Velocity Coefficient. If C_1 and C_2 represent the special concentration of gram molecules present, the velocity of the

reaction will be proportional to C_1C_2 or the velocity V of the reaction will be

$$V = C_1 C_2 k$$

where k is a constant or coefficient to be determined for the given temperature. This velocity of reaction will proceed each way in reversible reactions, the concentrations of the molecules in the reverse action being represented by C_1' and C_2' and the velocity of reaction by V', the velocity of the reaction in the reverse direction will be

$$V' = C_1' C_2' k'$$

where k' is the velocity constant to be determined for the reverse reaction.

The Equilibrium Constant. The chemical driving force for any reaction will continually diminish as the reaction approaches equilibrium, or the velocity of the reaction will diminish as equilibrium is approached, and when equilibrium is reached V will equal V' and

$$kC_1 C_2 = k'C_1' C_2'$$

This dynamic equilibrium indicates that as much reactive substance is being formed in a given time as is being decomposed, and a fixed relation therefore results, but the reactions have not ceased, only the velocities have equalized, and the driving chemical forces are incapable of making any further change in the reacting substances unless the velocity in one direction or the other is changed. In this state of equilibrium the ratio between the velocity coefficients or constants is

$$\frac{k_1}{k} = \frac{C_1' C_2'}{C_1 C_2} = K \text{ equilibrium constant.}$$

Or, as the concentration or active mass in any reaction increases, the velocity coefficient increases, and for each change in equilibrium due to temperature change there is a definite concentration ratio represented by this equilibrium constant K.

Partial Pressures. If the concentration of a given molecule is C and the collisions of the molecule are proportional to this concentration, if there are two molecules the collisions between

the two similar molecules will be C times as great as one molecule, or C^2. As the total pressure of a mixture of gases is the sum of the pressure of each gas, and by Avagadro's hypothesis the pressure is proportional to the number of molecules in the given space, the concentrations instead of being represented by gram molecules C may be expressed as partial pressure p, and equilibrium will be represented by the ratio of the partial pressures of the gases. Thus two molecules of NO will have the pressure p^2_{NO} while p_N and p_O may represent the pressure of N and O. At equilibrium the constant K will then become

$$K = \frac{p^2_{NO}}{p_N\, p_O}$$

and for any pressure and volume the familiar equation

$$PV = RT$$

will represent the work done. Where P is the pressure, V the volume, R the gas constant, and T the absolute temperature. The work done in the reaction

$$N_2 + O_2 = 2NO$$

will consist in taking one molecule of N from the pressure p and transferring to the pressure P also one molecule of O from the pressure p, to pressure P, and offsetting this work will be the transferring of two molecules of NO from pressure P_{NO} to p_{NO} when the pressure of a gas at constant volume is increased by the infinitely small amount dp, the corresponding work done dA will be

$$dA = dpV$$

The Maximum Work. If we substitute for V its value from the equation

$$pV = RT$$

we have

$$V = \frac{RT}{p}$$

and

$$dA = \frac{RT\,dp}{p}$$

and for the work done between the limits of pressure p and P we have

$$A = RT \int_{P}^{p} \frac{dp}{p} = RTln \frac{p}{P}$$

where ln is the natural logarithm. For the work done in forming the NO at a temperature T, we will have

$$A = RTln \frac{p_N}{P_N} + RTln \frac{p_O}{P_O} - 2RTln \frac{p_{NO}}{P_{NO}}$$

or simplifying and assembling the initial pressures and the final pressures in separate terms, we have for constant temperature

$$A = RTln \frac{p_N p_O}{p^2_{NO}} + RTln \frac{P^2_{NO}}{P_N P_O}$$

But the first term represents the initial pressures or the work done on the initial condition of the materials, and we are not called upon to furnish this energy, the change of energy being represented only by the second term

$$RTln \frac{P^2_{NO}}{P_N P_O}$$

This quantity $\frac{P^2_{NO}}{P_N P_O}$ is, however, the ratio of pressures or concentrations represented by the equilibrium constant K and hence the work done at any given temperature may be represented by the equation

$$A = RTlnK$$

Van't Hoff has applied this type of fundamental equation to a wide range of reactions, and by means of the second law of thermodynamics has made it applicable to temperature and concentration changes in which the latent energy plays an important part, for in these reactions the product of the specific heat by the temperature no longer represents the heat transfer.

Van't Hoff's Fundamental Equation. The second law of thermodynamics expresses the relation of A, the maximum work

possible at a temperature T, and U, the decrease in energy of the system in relation to the ratio of change of A with the temperature T, the equation being

$$A - U = T \frac{dA}{dT}$$

Substituting in this the value of A and $\frac{dA}{dT}$ obtained from the equation

$$A = RTlnK$$

we have when both A and lnK change with the temperature T

$$\frac{dA}{dT} = RLnK + RT \frac{dlnK}{dT}$$

and hence

$$U = - RT^2 \frac{dlnK}{dT}$$

which is van't Hoff's fundamental equation for chemical reactions in which the heats of reaction U are important factors, and both the temperature and concentrations may be variable. The quantity U, which in thermodynamics represents the decrease in energy of the system, may here represent the energy of chemical combination, which changes very little with changes of temperature and is generally designated as Q, and in the case of nitric oxide it has the value 21,500 calories per gram molecule; so the equation becomes

$$43{,}000 = - RT^2 \frac{dlnK}{dT}$$

and when using the air as a source of nitrogen in which the nitrogen content is 79.2 percent and the oxygen 21.8 percent and letting x represent the percentage of NO formed, as $\frac{1}{2}x$ will be from the nitrogen and $\frac{1}{2}x$ from the oxygen, the equilibrium constant K will be

$$K = \frac{x^2}{\left(79.2 - \frac{x}{2}\right)\left(20.8 - \frac{x}{2}\right)}$$

Nernst's Determinations of Equilibrium. Nernst and his assistants determined x for a number of temperatures, the calculated and observed values being as follows:

T	X (Obs.)	X (Calc.)	Observer
1811	0.37	0.35	Nernst
1877	0.42	0.43	Jellinek
2023	bt. 0.52 and 0.80	0.64	Jellinek
2033	0.64	0.67	Nernst
2195	0.97	0.98	Nernst
2580	2.05	2.02	Nernst-Finckh
2675	2.23	2.35	Nernst-Finckh

Nernst's calculations of x or equilibrium volumes in percent of NO, using air at temperatures of 1,500 deg. T to 3,200 deg. T are plotted in Fig. 1.

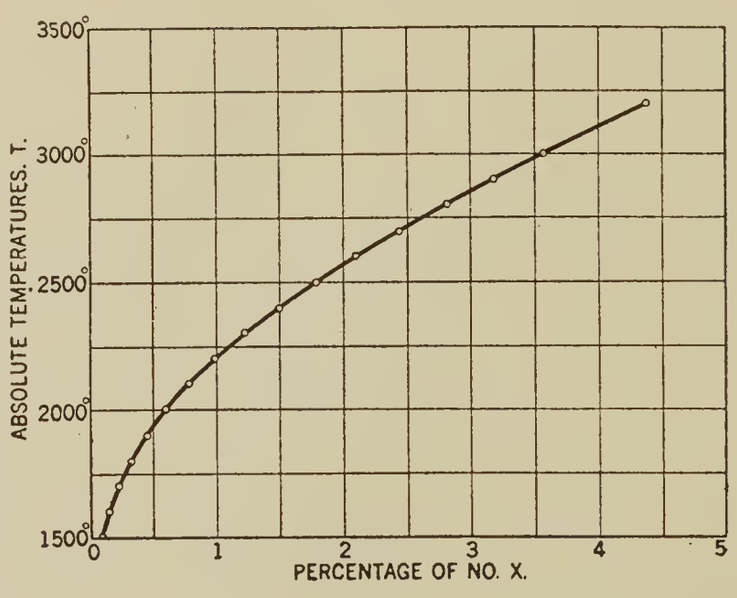

FIG. 1.

Rapidity of Dissociation. Nernst and Jellinek also determined the rapidity with which the NO is decomposed or dissociated at the various temperatures, and these experiments showed that the tendency of NO to revert to molecular N and O is very slight below a temperature of 1,500° C., but increases very rapidly with the temperature, so that the time of withdrawing the products through the varying zones of heat in the electric arc is sufficient to effect a large amount of dissociation. In order to avoid this dissociation a rapid movement of the air through the arc or the arc through the air is desirable, and this in turn causes increased radiation and convection losses,

so the maximum possible temperature of the arc is not obtained, and hence there are imposed very distinct limitations to the yield of NO.

Haber's Theory of Ionic and Electronic Collisions. Haber and Koenig investigated the possibility of utilizing lower temperatures in the arc to avoid dissociation by enclosing the arc in a water-cooled quartz tube, whereby moderate temperatures were preserved. In place of the molecular collisions we have assumed above as due to the thermodynamic condition of the gas, they used a vacuum and endeavored to utilize the kinetic energy from the rapid motion of the ions and electrons liberated by the arc stream under these conditions. Haber considered it possible to increase the thermodynamic concentrations about 50 percent. His tests indicated that using a temperature of 3,000 deg. cent. it was possible to show 10 percent concentrations of NO, which would correspond to a temperature under the thermodynamic equilibrium of 4,300 deg. cent. Haber gives a table showing the effect of various mixtures of N and O when working with the increased mean free path of the molecules due to a vacuum of 100 mm. of mercury. In his work Haber prefers to use the square root of the equilibrium constant K we have used above, thus enabling the partial pressures of the resulting substances to be read direct, while the partial pressures of the ingredients are expressed as square roots of the pressures.

Haber's table for a pressure of 100 mm. is as follows:

Gas Mixture				$K = \frac{(NO)}{(N_2)^{1/2}(O_2)^{1/2}}$	Thermodynamically Calculated Absolute Temperature by	
	O_2 Percent	N_2 Percent	Percent NO		Haber	Nernst
Air	20.9	79.1	9.8	0.284	4365	4334
Half-half Mixture	48.9	51.1	14.4	0.337	4686	4650
	44.4	55.6	14.3	0.337	4686	4650
Reversed Air Mixture	75.0	25.0	12.8	0.357	4805	4767
	81.7	18.3	12.1	0.397	5042	5000

The yields of NO per kilowatt hour obtained by Haber were unsatisfactory, and the complications of small water-cooled tubes and working under a vacuum of 100 mm. have not justified commercially the higher concentrations of NO he obtained.

Commercial Processes Now in Use Have Distinct Limitations. We may assume that up to the present the processes in commercial use are limited strictly by the thermodynamic equilibrium of the van't Hoff equation. As the volume of gases when working with low concentrations of NO are considerable, the radiation and convection losses as well as the transfer of sensible and latent heat from the arc to the gases lower very materially the temperature of the arcs, and the yields therefore indicate an average working temperature of 2,200 deg. cent. to 2,500 deg. cent., or concentrations of 1.5 percent to 2 percent NO when working with air. These theoretical limitations of the direct process of forming NO have therefore led to many efforts to dissociate the nitrogen molecule by other means.

Sources of Chemical Energy. Naturally the sources of chemical energy have offered a most fruitful field, but, like the synthesis of carbon compounds, a considerable elevation of temperature is necessary before the chemical energy becomes effective enough to break the bond of the nitrogen molecule. At these elevated temperatures practically all elements or compounds which release sufficient energy to combine with nitrogen have a greater combining power for oxygen, so the processes cannot be conducted with air, but involve the separation of the nitrogen from the oxygen of the air as a preliminary step. The compounds of nitrogen thus formed do not therefore include the oxides of nitrogen. The common elements exhibiting the most pronounced tendency to combine with nitrogen are calcium (Ca), magnesium (Mg), aluminum (Al), boron (B), etc. The carbides of a large number of metals also exhibit a pronounced tendency to combine with molecular nitrogen when heated.

The great advantage from a theoretical standpoint in utilizing these processes is that the reaction with nitrogen may be made more complete as equilibrium may be continually disturbed by withdrawing the compound of nitrogen formed or by presenting to the nitrogen to be combined fresh combining surfaces of the substance, and the action may be caused to proceed practically quantitatively, thus avoiding heating large quantities of materials which are inert to the reaction. A vast field of research is opened by these possibilities, as very few of the equilibrium figures have been determined, and it is almost certain that direct

combustion methods may eventually be evolved along these lines.

The experimental data are so meager that no theoretical limitations can be placed. The reactions assume unusual importance however on account of a wide application in the arts. This may be best illustrated by considering the formation of calcium carbide, CaC_2, in relation to its three reversible reactions, namely,

$$(1)\quad CaO + 3C \leftrightharpoons CaC_2 + CO$$
$$(2)\quad CaC \leftrightharpoons Ca + C$$
$$(3)\quad CaO + C \leftrightharpoons Ca + CO$$

There are here six substances, some in solid form, some in liquid and some gaseous (molecular and atomic), and it is evident that the temperature will have a marked influence on the equilibrium which will exist, and the reaction will be greatly affected by very minute changes, for the partial pressure of the gases will be suddenly changed by such conditions as the carbon released in a gaseous state immediately combining to form amorphous carbon, or the metallic calcium vapor combining with the oxygen released by the CO to form calcium oxide, which immediately precipitates as a solid. The fact that calcium oxide, which is most refractory, can be vaporized at a temperature of 1,600 deg. cent. to 1,800 deg. cent. in the sense that the calcium is vaporized and decomposes CO to again precipitate CaO, is one of the actions similar to the fumes in smelting furnaces which accounts for a heavy loss of metal at temperatures not ordinarily capable of producing vapors. When nitrogen is inserted in a reaction of this kind, there are immediately formed complex carbon-nitrogen compounds, but the action of the oxygen present is to dissociate these, allowing the nitrogen to combine into the molecular form and the metal to precipitate from the fume as a minute particle of metallic oxide, the carbon precipitating as amorphous carbon in the form of soot, as all of these reactions liberate a large amount of energy. The temperature of these reactions is from 1,500 deg. cent. to 2,000 deg. cent., and is therefore well within the range of combustion methods if the combustion could be in contact with the substances as in the blast furnace, but the presence of the oxygen necessary for combustion prevents the formation of nitrogen compounds.

The effect of partial pressures in these reactions is of fundamental importance. The active mass of a solid is constant, and hence at the boundary surface where the solid and gases meet there is a high velocity of reaction. Equilibrium will be produced either by the solid forming a coating of the compound which will place it in equilibrium or by the pressure of the gases generated from the reaction producing a condition of equilibrium. Taking the familiar calcium carbonate reaction as an illustration,

$$CaCO_3 \leftrightharpoons CaO + CO_2$$

There being two substances in the solid state and one in the gaseous, the equilibrium constant K will be

$$K = \frac{CaO \times CO_2}{CaCO_3}$$

where CaO and $CaCO_3$ are the very slight vapor pressures of the solids; that is, the sublimation pressures, which in practice are too small to measure. The pressure of the CO_2 will be practically the total pressure, and as this varies, the velocity constant K will vary and hence for any temperature there is but one pressure for equilibrium. LeChatelier measured the temperatures and pressures of the above reaction over a wide range and found a variation in the temperature necessary to produce the reaction of from 547 deg. cent. at 27 mm. pressure to 865 deg. at 1,333 mm.; or in other words, equilibrium could be produced through a range in temperature of 60 percent., and at one point a change of two degrees necessitated a change in pressure of over 10 percent. in order to restore equilibrium. Rothmund found the equilibrium pressure of CO in the carbide of calcium reaction to be 250 mm. at 1,620 deg. cent. If the CO pressure was raised above the equilibrium figure at this temperature, CO was absorbed and no carbide was formed. By inserting inert gases so the CO was diluted and its partial pressure reduced, the temperature of the formation of carbide was varied over 20 percent. These results all indicate that for the nitrogen reactions, the actions and reactions must not only be subject to accurate temperature regulation, but the partial pressures must be controlled, and it is probable that definite zones of reaction must be maintained. The present commercial applica-

tions such as the Serpek and cyanamid processes prepare the compounds of nitrogen by causing the nitrogen to react largely with the solid masses and thus avoid many of these complications due to the vapor processes, or variable minute pressures of sublimation.

By substituting the resistance furnace for the arc and reducing the metals in the presence of nitrogen, thus forming nitrides or forming carbides, and treating these in the presence of nitrogen, there have been developed a number of processes which have been commercially applied.

III—Description of Processes

Three processes which have been commercially applied for directly preparing nitric acid from atmospheric nitrogen are: first, Birkeland-Eyde; second, the Schonherr, and third, the Pauling. These are diagrammatically shown in Figs. 2, 3 and 4. Fundamentally all operate on the same principle of forcing air into intimate contact with a high-tension arc and withdrawing the product nitric oxide, NO, as directly and rapidly as possible in order to reduce the amount of decomposition of the resulting product. As these processes have been repeatedly described in detail in the technical press, we will confine our attention to general comparisons.

Birkeland-Eyde Process. The Birkeland-Eyde furnace, illustrated in Fig. 2, has been the most extensively used. Its most distinctive features are the use of the magnets *A,* which distort the arc into a series of great wheels of flame, extending radially outward from the electrodes *E,* located normal to the paper in Fig. 2. The air enters through the conduit *C* and is distributed to the arc through the holes in the firebrick lining. The products are withdrawn from around the periphery at *D*. The voltage of 10,000 volts is reduced by an inductive reactance coil to about 5,500 volts across the electrodes. The alternating current of 50 cycles establishes the arc across the *U*-shaped water-cooled electrodes *E,* spaced about 0.3 in. (8 mm.) apart, and a flow of current takes place across this ionized path, the electrons formed being repelled by the intense magnet field of the direct-current magnets, *A,* and their discharge radially outward causes the arc stream to follow until it is deflected outward in a great

semicircle. As its length is thus increased, the potential across the electrodes rises and a second arc is established, the effect being to make a series of rapidly expanding arcs which are expanded across the entering air spaces. As the arcs travel radially outward, the contact of the ionized arc stream with the incoming air disrupts the nitrogen molecule and causes the formation of NO, and the gaseous products travel rapidly to the periphery

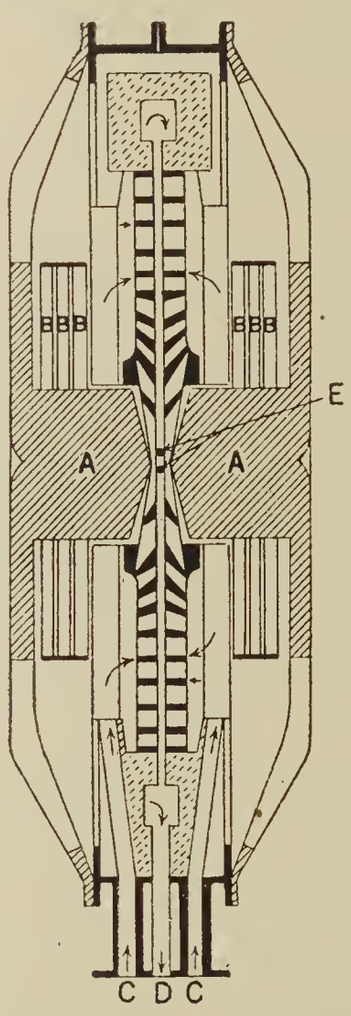

Fig. 2—Birkeland-Eyde Furnace
A, core; B, windings; C, gas entrance; D, exit

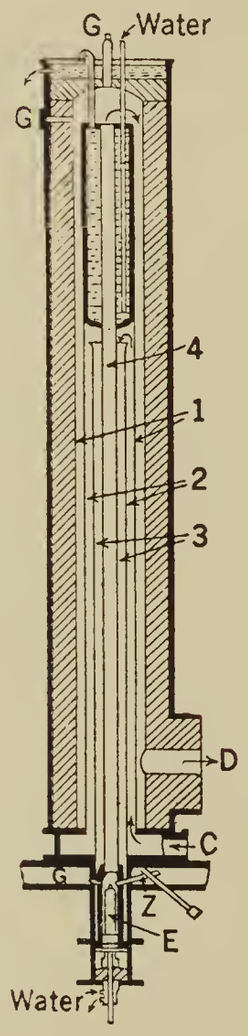

Fig. 3—Schonherr Furnace

of the furnace, where they are withdrawn at an average temperature of about 1,250 deg. cent. The earlier Eyde furnaces were of 300 kw. capacity and gave a concentration of about 1.5 percent NO and a yield of about 500 kg. of nitric acid per kw. per year. The more recent furnaces are of 3,000 kw. capacity and give concentration of about 2 percent NO and a yield of 580 to 600 kg. of nitric acid per kw. per year, or 65 to 70 grams of nitric acid per kw.-hr.

Schonherr Process. The Schonherr furnace (Fig. 3) consists of a long iron pipe, having an electrode *E* inserted in the bottom, and the tube itself is the other electrode, the distinctive feature of the process being that an alternating current at 4,500 to 5,000 volts maintains an arc of from 23 to 25 feet (7 m. to 8 m.). The furnace is started by forming an arc from the lower electrode to the wall of the iron pipe by means of a lever *Z*, a blast of air is then admitted to the pipe, whereupon the ionized gases are caused to ascend and carry with them the arc stream. In this way the arc is caused to travel toward the upper end of the tube, where it is maintained. In practice, the air stream is ad-

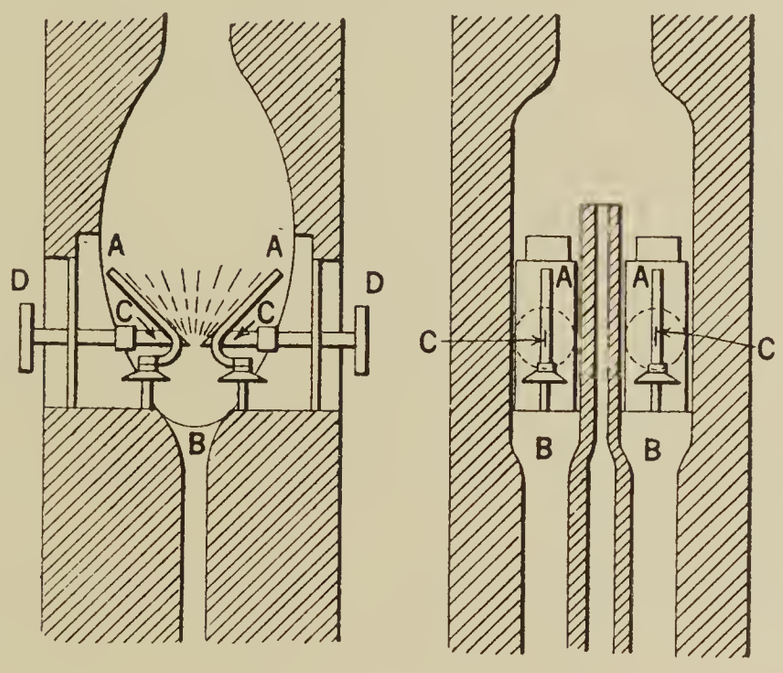

FIG. 4—PAULING FURNACE

mitted in a tangential direction, causing a whirling motion to be imparted to the air surrounding the arc; this creates a vortex motion, causing the arc to be surrounded by the cooler air and thus protects the iron pipe which is wholly unlined. The rapid passage of the air maintains an ionized path for the arc stream, and the arc burns quietly. The products are withdrawn from the upper end and pass downward through the passes *I* to the outlet *D*. Previous to being withdrawn they are cooled by the water cooler and are further used to preheat the entering air. The temperature of the exit gases is about 850 deg. cent. Provision is made for preheating the air by passing it upward in the space 2 of the casing and then downward to a point opposite

the electrode. The largest furnaces are of 800 kw. capacity and maintain an arc about 23 ft. (7 m.) long. They give an NO concentration of about 2.25 percent and a yield of 550 to 575 kg. per kw.-year or 65 grams per kw.-hr.

Pauling Process. The Pauling furnace (Fig. 4) establishes an a-c. arc of 4,000 volts between two curved horns, much after the pattern of the horn type lightning arrester. This arc when established is driven upward by a blast of air admitted at *B* and is disrupted by the diverging horns. A sheet of arc flame is maintained by re-establishing a new arc, as the previous one is elongated. The effect is to create an arc flame about 30 in. (75 cm.) high and to have this flame in intimate contact with the rapid moving air used to blast the arc flame. Two furnaces are usually operated together, and to assist in a rapid cooling of the products, a portion of the previously heated or partially cooled discharged gases are admitted to the top of the furnace. The arc is established by the high voltage breaking down the gap between narrow blades *C*, located in the horn gaps, and as these wear away, they are continually advanced by the adjustments *D*. The percentage of NO obtained is 1.25 to 1.5 percent in the 400 kw. furnace, while the yields are 525 to 540 kg. per kw.-year or 60 grams per kw.-hr.

Power Factor and Electrode Wear. In all these processes where the arc is distorted the power factor is about 70 percent, being about 5 percent lower in the Schonherr type, apparently due to inductive effects of the iron pipe surrounding the arc. In both the Pauling and Schonherr furnaces the electrodes are adjustable and the air blast plays directly on the electrodes, necessitating this adjustment and also means of easy renewals. The Pauling blades last less than twenty-four hours. The Schonherr electrode is a straight rod of iron and is fed upward as it burns away. The Eyde water-cooled copper pipe not being directly in the path of the air blast lasts three to four weeks. In the operation of both the Eyde and Schonherr furnaces a furnace is placed on each separate leg of the three-phase circuit, so that six wires are used for each generator. In the installations that have been made the furnaces are connected direct without transformers, and as no parallel operation of generators is at-

tempted, a large number of cables are required between the power house and the furnaces.

Efficiency and Losses. It will be noted that notwithstanding the radically different types of these furnaces there is not a wide divergency in the yields, the Schonherr furnace showing the highest concentration of NO, while the Eyde probably produces a slightly higher output per kw.-hr. All of these concentrations indicate that the maximum temperature of the arc is not utilized, but is very considerably reduced by the large amount of air admitted. If the temperature of the arc is raised by admitting less air, there is a heavier decomposition of the products, and all products are heated to a higher temperature with a corresponding loss, the net result being a lower yield per kw.-hr. As the yield per kw.-hr. is of fundamental importance, adjustments are governed accordingly. The concentration of NO affects directly the apparatus for recovering the products, such as the absorbing towers, and the lower the concentration of NO the greater the losses from heating the inert gases. The furnace efficiency will largely be determined by this factor. Let us take for example a concentration of 1.75 to 2 percent NO and examine the distribution of heat. If we take the specific heats of a molecule of the diatomic gases as constant, there will be no difference in the specific heats per molecule of N, O or NO, and taking a standard value for this, we may calculate the heat energy expended. Let us assume, following Haber, that for a change of temperature t, the specific heat per molecule will be

$$6.8 + 0.0006\,t$$

The gaseous products heated in the furnace with 1.75 to 2 percent NO concentrations will have, from Nernst constants, an absolute temperature of about 2,500 deg., and the air would have an initial temperature say of 27 deg. cent. or 300 deg. absolute, so the arc would raise the temperature of the 100 molecules through 2,200 deg., or,

$$\begin{aligned}\text{sensible heat} &= 100\ (6.8 + 0.0006\ t \times 2{,}200)\ 2{,}200 \\ &= 1{,}786{,}400 \text{ calories}\end{aligned}$$

As two molecules of NO require a latent heat of formation of 43,000 calories, the total heat will be 1,829,400 gram-calories;

and as one watt hour equals 860 gram-calories, the energy represented will be equal to 2.12 kw.-hr. for two gram-molecules of NO. Taking the atomic weight of N as 14 and of O as 16, the gram-molecule of NO will weigh 30 grams, so 2.12 kw.-hr. will form 60 grams of NO.

If we mix this NO with air and water it will form nitric acid without requiring a further expenditure of energy, thus,

$$2NO + 1\tfrac{1}{2}\,O + H_2O = 2HNO_3$$

and the 60 grams of NO will then become 126 grams of HNO_3; the production of nitric acid will then be 126 grams per 2.12 kw.-hr. or 59.4 grams of HNO_3 per kw.-hr. Of this expenditure of 2.12 kw.-hr. the formation of the nitric oxide utilized

$$\frac{43000}{1,829,400} = 2.35 \text{ percent}$$

and the sensible heat imparted to the active gases to raise their temperature to form two molecules of NO required 35,728 calories, so this represented

$$\frac{35,728}{1,829,400} = 1.95 \text{ percent}$$

while the heating of inert nitrogen and oxygen, or that portion of the air which was not utilized, but which was heated to the furnace temperature, was represented by

$$\frac{1,750,672}{1,829,400} = 95.7 \text{ percent}$$

These calculations, while open to some criticism on account of the uncertainty of the figures for specific heat and its change with temperature, closely approximate the conditions, and indicate that low concentrations of NO, when formed from thermal reactions, are extremely wasteful. If concentrations of 10 percent NO are obtained with temperatures of 4,200 deg. to 4,300 deg. cent., the yields may be increased to 135 to 140 grams of HNO_3 per kw.-hr., but the greatest saving in energy will result in utilizing other than purely thermal energy. While thermal energy may be produced more cheaply directly from fuel, its temperature possibilities are again limited by the inert gases of combustion if air is the source of these.

Hausser has commercially applied a process for utilizing coke oven gases by means of an explosion bomb. The amounts of excess gases may be limited, and the intimate mixture of combustible and oxygen due to pre-compression of the charge permits of high combustion temperatures being reached. Fig. 5 shows this bomb having a capacity of 1,600 cu. cm. The gases, either illuminating or coke oven gases, enter through the inlet after previously exhausting the air by means of the air pump outlet. Means are provided at *A* for injecting under high pres-

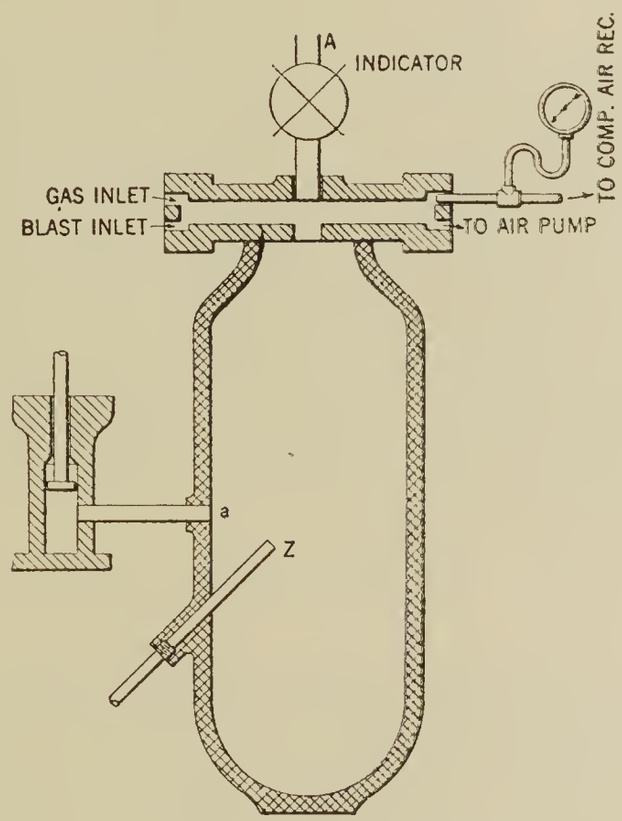

FIG. 5—HAUSSER PROCESS

sure a spray of water to cool the products as quickly as possible. The ignition takes place at 2 by means of a high-tension spark, and the explosion is propagated outward from this point and the vapor condenses on the enamel lining of the bomb.

With this device Hausser obtained a temperature of 2,100° K. and concentrations of NO of 0.5 percent. The temperature calculated from the assumed figures for specific heat indicated a concentration of 0.3 percent for equilibrium by the Nernst calculation, and Hausser sought to explain this increase of yield as due to a chemical reaction induced by photo-chemical effects similar to the ionization by ultra-violet or actinic rays of light.

The maximum yields were 99 grams of HNO_3 per cu. m. of gas, or equivalent to 6.2 lb. of HNO_3 per 1,000 ft. of gas. A commercial plant on this system has been installed in Germany. This low concentration of NO greatly complicates the commercial application, as the absorbing devices are more cumbersome and the percentages of loss are higher.

Method of Utilizing NO. All of the above nitric acid processes utilize the reaction

$$2NO + O_2 \leftrightharpoons 2NO_2$$

which is an exothermic one for the formation of the peroxide, and if the temperatures are controlled, side reactions can be prevented and equilibrium can be maintained with only a small percentage of NO remaining. The gases, after leaving the furnaces, are usually carried through waste heat boilers where 50 to 60 percent of the heat is utilized for steam production. They are then cooled in aluminum pipe coolers and allowed to enter a gas holder, where time is given to form the peroxide. The products then enter counter current absorption towers, where the reaction with water forms

$$2NO_2 + H_2O = HNO_3 + HNO_2$$

the nitrous acid, HNO_2, is further oxidized and utilized to form HNO_3 in contact with the excess oxygen in the gases and with the absorbing water. The final recovery is usually made by circulating the gases through two towers of weak alkaline solution, such as sodium carbonate, and this is converted into sodium nitrate and into sodium nitrite, and recovered by evaporation; the final products are a combined nitrate-nitrite of sodium. A normal circulation over three absorbing towers gives an acid of about 30 percent concentration, but this can be increased to 45 or 50 percent by recirculating over the first tower. Further concentrations are usually made by evaporation. All of these processes are simplified by increased concentrations of NO in the initial reaction. About two to three percent of the original NO is discharged in the waste gases from the absorbing towers. It will be noted that one great advantage of these processes is that they require the handling of only air, gas and water up to

the time the nitric acid is formed in the absorbing towers, so that the simplest handling devices suffice and the labor is a minimum; also no chemicals are required until the final washing with the alkaline solution in the absorbing towers, and this may be a cheap solution, such as lime water, if conditions make it desirable.

Cyanamid Process. The very low yields, representing less than 5 percent of the energy expended and amounting to 65 kw.-hr. per kg. of N fixed, naturally have turned attention to chemical reactions as a means of increasing the yields. One of the most important of these is the process for making cyanamid, $CaCN_2$. As a separate paper is to be presented here covering this subject, we will only generalize.

The endothermic reaction and the heating of the materials entering into the calcium carbide reaction have an approximate theoretical value of 3.1 kw.-hr. per kg. produced, whereas it requires about 4 kw.-hr. to produce a kg. of 85 percent calcium carbide in the best practice. For 100 percent carbide it would require 4.7 kw.-hr., and the efficiency is therefore,

$$\frac{3.1}{4.7} = 66 \text{ percent}$$

The union of carbide and nitrogen is exothermic when a sufficient temperature is reached, so the actual expenditure of energy for this reaction is not in excess of 0.1 to 0.2 kw.-hr. additional for the fixation of the nitrogen. We require further the preparation of the nitrogen and the grinding of the carbide to prepare it for the nitrogen treatment. The cyanamid can be used directly in the fertilizer industry, but for use in the chemical industries it must be decomposed to form ammonia; or, if nitric acid is required, it must be made from the ammonia by some process such as the Ostwald contact process. We may figure, however, that the yield for a given amount of electric energy, which amounts to about 16.6 kw.-hr. per kg. of N fixed, is from four to five times the yield of the direct nitric acid processes, while offsetting this is the cost of preparing the nitrogen, the cost of chemicals, the handling of materials at high temperature and the many factors making up manufacturing costs.

The Serpek Process. The Serpek process is typical and has been quite extensively introduced commercially. The reaction is represented by the equation

$$Al_2O_3 + 3C + N_2 = 2AlN + 3CO$$

The reacting temperature for best results is claimed to be 1,800 deg. to 1,900 deg. cent., but no effort is made to define the equilibrium conditions, and it is very evident that where CO enters so actively into the reaction, the temperatures can be materially altered by a change in the partial pressures of the N and CO. One of the most interesting features of this process is that the impure Al_2O_3 in the form of bauxite is fed into the furnace together with coal and the sensible heat is therefore partially derived from the coal. Neglecting the specific heats of the solids, the endothermic reaction requires three kw.-hr. per kg. of aluminum nitride, having an approximate content of 26 to 34 percent N; it would require therefore 9 to 10 kw.-hr. per kg. of N under the best conditions if the coal and producer gas were capable of supplying all the heat energy required to produce the required temperature in the gaseous and solid products. In the case of cyanamid it requires about 4 kg. of high-grade carbide per kg. of nitrogen, or a kg. of N requires 16 kw.-hr. under favorable conditions and about 0.2 kw.-hr. for heating the carbide against 10 to 12 kw.-hr. in the Serpek process. If all energy were supplied from the electric source, the Serpek process would require practically the same electrical energy as the cyanamid process.

There is a distinct advantage in being able to use producer gas in place of preparing purified nitrogen, and there is a further advantage in conducting the process with one operation. In practice Serpek uses a revolving barrel furnace of the resistance type, the resistance consisting of a squirrel-cage construction which continually agitates the material as it passes through. In all nitride reactions this is essential, as the materials become coated with a covering which protects the interior and prevents further absorption of nitrogen. Serpek feeds bauxite and coal from a producer type of furnace into this revolving electric furnace and the sensible heat is thus utilized to heat the mate-

rial as it travels to the electric furnace; the product is discharged from the electric furnace as aluminum nitride, with a content of 26 percent to 34 percent N.

The aluminum nitride can be treated with steam and the N converted into ammonia, or the ammonia may be converted into nitric acid. Serpek claims a process for converting the nitride directly into nitric acid, but no details are available. One drawback to using bauxite is that the resulting aluminum oxide is more difficult to use than the impure bauxite and the process does not work as economically. It is probable that some cheap catalytic agents may be found to substitute for the bauxite, but otherwise the Serpek process should necessarily find its greatest application in connection with the reduction of aluminum.

Haber Catalytic Process. One other process which has attracted marked attention on account of the scientific eminence of its inventor, as well as the commercial results obtained, is the Haber process for the synthesis of ammonia directly from its components N and H. This means that there must be a supply of these elements available or they must be cheaply produced. The reaction is an exothermic one producing 11,000 calories per gram-molecule, so the problem is not so much the energy consumption as the peculiarities of the reaction

$$N_2 + 3H_2 = 2NH_3$$

The ammonia formed is practically decomposed at 750 deg. cent. It has been difficult to get any substance to react with the N at this low temperature, and, while the nitrogen was made active toward many substances, it was easy to decompose the resulting NH_3 into its constituent molecules, and all yields obtained were too low to justify commercial results. Haber's success seems due more to ingenuity in constructing his apparatus and to the discovery of a suitable catalyzer than to any departure from previously known principles. The fact that one molecule of N and three of H form only two molecules of ammonia indicates that the volume occupied by the ammonia will occupy only one-half the space occupied by its constituent gases, and hence this contraction of volume will be assisted by pressure. Haber increased the pressure on the reacting gases to 200 at-

mospheres, and as a catalyzer he used uranium. He found at 500 deg. cent. he could react on the nitrogen and upwards of 8 percent of ammonia could be formed before equilibrium took place. By using limited amounts of N and an excess of H the equilibrium pressures were adjusted well within the decomposition limits of temperatures, and by withdrawing the gases from the catalyzer as they reached equilibrium the process was made continuous. The fact that decomposing ammonia creates a most destructive corrosive agent had to be met, and the retorts had to be made strong enough to stand the effects of the high pressure and also possible explosions, as hydrogen compressed to 200 atmospheres and heated to 500 deg. cent. is a most active agent in the presence of impurities such as oxygen, sulphur, etc. The retorts can be made of very moderate size and a number of them used, and by heating internally with electric resistance the shells are not subjected to the effects of temperature, so the process seems to have met with very pronounced technical success. The consumption of energy for heating the gases is very slight, as the exothermic reactions will compensate largely for the heat required to release this.

The preparation of the N and H and the compression to 200 atmospheres will represent the greatest costs of production. It will be noted that all products are handled in the gaseous condition, being most favorable for low labor costs. The ammonia is extracted from the mixture of N and H by slightly cooling the gases until the point of liquefaction of ammonia is reached and the ammonia condenses out. The remaining gases are passed back to the retort without sacrificing the original pressure of compression. The work done on the gases is thus reduced to a minimum, and equilibrium can be continually disturbed by withdrawing the products without heavy losses. This process involves the expenditure of approximately 1.5 kw.-hr. per kg. of N and therefore represents the lowest consumption of energy of any of the fixation processes.

From an engineering point of view the various processes must be considered from other than the technical standpoint, the question of particular application being the guiding consideration in most cases.

IV—The Economics of Nitrogen Fixation

Fertilizers. In considering nitrogen fixation and its relation to fertilizers we must remember it is only one of the three important ingredients of fertilizers, the other two being phosphorus and potassium. It is possible to obtain nitrogen from the atmosphere and transfer it to the soil by means of nitrifying bacteria, which may be cultivated by such plant life as the legumes, to which family belong the clover and alfalfa. These plants have a nodule on the stem which is the seat of the bacteria activity, and if the plants containing this nitrogen are returned to the soil, the soil may be enriched in nitrogen, but the crop must be sacrificed or partially so. When it is not desirable to plant these nitrifying crops, recourse must be had to nitrogen in the form of fertilizer. Unfortunately all crops deprive the soil of fertility, and in the case of phosphorus and potassium converted into the crops, these must actually be replaced or barren soil will eventually result. Each soil must be treated for the particular crop it is to bear, and usually there are fixed mixtures which become standard for various crops. These mixtures contain the nitrogen, the phosphorus and the potassium in varying amounts. The output of nitrogen from a chemical works would ordinarily be shipped to these fertilizer manufacturers unless the chemical works desired to manufacture the mixed fertilizers.

Of all the processes we have considered, the cyanamid is the only one which manufactures a product which is in a form to go into the fertilizer market direct. The nitric acid processes must unite the acid with some alkaline base such as sodium, lime or ammonia, and the ammonia processes must unite the product with an acid such as sulphuric or nitric. The nitride processes can hardly afford to ship the nitride, as it is combined with an ore or base such as aluminum oxide, which may be more desirable in the aluminum industry, as the fertilizer industry will pay only on a nitrogen basis.

Price of Nitrogen. In general the price of combined nitrogen, as we have seen, is fixed by the price of Chile nitrate. Thus if this sells for two cents per lb. and contains 15 percent N, the price per lb. of N is 13.2 cents, and this in turn would make

the price of ammonia sulphate, having 21 percent of nitrogen, 2.7 cents per lb. These have been current prices. In considering the production of nitrogen products, it would seem that, while these prices control nitrogen for the fertilizer industry, it would be desirable to produce if possible products which are manufactured from these crude products and thus avoid competition with the natural products direct. Nitric acid of commerce is manufactured from soda nitrate by treatment with sulphuric acid, about 72 percent of the sodium nitrate being nitric acid. As the by-products of this operation only partially pay the costs, the manufacturing costs leave the nitric acid with a value of 50 percent over the value as nitrate. Hence a chemical works could afford to produce nitric acid when they could not afford to add a manufacturing cost to produce a fertilizer from the nitric acid and then sell it in competition with the crude Chile nitrate.

A large portion of the phosphate rock of this country is treated with sulphuric acid to form the so-called superphosphates. If nitric acid is used in place of sulphuic acid, the superphosphate can be produced at the same time as a fertilizer of lime nitrate, or, if preferred, a high concentration of phosphoric acid can be produced from lower-grade phosphate rock. Industries of this kind promise more favorable results commercially than does the direct production of fertilizer. If low-grade products are manufactured at close prices, a very large volume of business is a necessity, and works of this character and magnitude are more apt to be a result of successful development rather than an initial venture in a field beset with uncertainties as to the profits and the chances of a development of other processes reducing these if they are problematical.

Costs of Making Products. Let us consider more in detail some of the costs. We may assume approximately that the labor and repairs in furnace room and absorbing tower will cost $10 per ton of nitric acid, and if nitric acid is selling for $60 per ton, we have a margin for power cost, interest, general expense, etc., of $50, and if we produce 500 kg. of acid per kilowatt year, it will require two kw.-yr. per metric ton or $25 per kilowatt-year, and we must absorb all interest charges and general expense in this. If the yield can be made 550 kg. per kilo-

watt-year and we can sell for $60 per short ton, we will require 1.8 kw.-yr. or $28 per kw.-yr. We must assume that the product does not have to be packed for shipment and that there are no selling costs involved, and we must figure on an output so that our units may be large enough to bring the investment in plant down to $80 per ton of acid, so the annual charge may be $8 or net $20 per kilowatt-year, and if $5 are allowed for general expense, the best we can do will be about $15 per kilowatt-year.

We see it would be hopeless to attempt to put this acid into a product to compete with the fertilizer prices, for they are some 50 percent lower in selling price, and it will involve a cost for some raw material to mix with the acid, the cost of manufacture and a packing and shipping charge. We must then abandon any idea of making fertilizer from nitric acid prepared by the direct oxidation of atmospheric nitrogen in the electric arc until such time as we can improve the very low efficiency due to the thermodynamic limitations of the reaction. We can only hope to utilize this process in the manufacture of nitric acid coupled with some other product which will procure for it a higher price. There is, for example, a limited demand for the nitrite of sodium $NaNO_2$ used in the dye industry, and this is manufactured by reducing nitric acid with molten lead, thereby adding another manufacturing operation to the acid cost. This nitrite may be cheaply made by taking a mixture of NO and NO_2, such as we would have in parts of the system, and passing it into water or sodium hydroxide, thus

$$NO_2 + NO + H_2O = 2HNO_2$$

or,

$$4NO + 2NaOH = N_2O + 2NaNO_2 + H_2O$$

and this process would produce a product selling for four to five cents per lb. We must remember, however, that the price of nitric acid is not a fixture and that a cheap combined nitrogen fertilizer will cut the price of sodium nitrate and hence the price of nitric acid. We are confronted then with the fact that all processes will be affected by the success of any one process that is a large enough success to affect the market conditions of combined nitrogen and upset the ruling prices in the fertilizer

industry. It is useless to look only to cheap power as a solution of this problem, as the real solution is in the improvement of processes.

Let us roughly compare the power requirements of the processes as we have outlined them above, and we find

Direct oxidizing of atmospheric nitrogen 5 percent efficiency, yield at 550 kg. per kw-year, requires per kg. of N	65 kw.-hr.
Cyanamid process 66 percent efficiency in carbide 1 percent loss in heating to combine with N., requires per kg. of N	16.6 "
Also preparation of N.	
Aluminum nitride using coal to heat products to temperature of reaction requires per kg. of N	12 "
Catalytic method of combining N and H to form ammonia, requires per kg. of N	1.5 "
Also preparation N and H, refrigeration, and compression to 200 atmospheres.	

The general tendency abroad in figuring the cost of water power is to give only the operating costs, and from this one sees costs of producing power figured at from 50 cents to $1.00 per kilowatt-year, and in using these figures erroneous ideas have been widely circulated. In this country it has been standard practice to consider the investment in the power plant; that is, the cost of the development and the property as fixing very largely the cost of producing the power. It is quite common to have labor and supplies cost not more than one dollar per kilowatt-year, but this would not be considered as representing the cost of the power. Where a chemical industry owns the hydroelectric power plant as well as the chemical works, the foreign practice is inclined to consider the investment as a whole and apportion the costs of operation to the various departments, while interest on the capital is charged to the profits. The costs of producing power are therefore uniformly much lower than we are accustomed to figure on. There are many plants in operation in the chemical industries abroad whose real costs of producing power are no lower than many of the more favored locations in this country.

Off-Peak Loads. One of the chief interests in the chemical utilization of electrical energy is centered in the possibilities

of off-peak or off-season loads, as American plants generally have a certain proportion of power which can be disposed of to better advantage than selling the entire output as low-priced power to chemical industries. This off-peak power is difficult to utilize in furnace work, where the cooling of the furnace and its charge is an important factor both from the standpoint of cost and of output, and again, adjustments may be so disturbed from an interrupted output as to be absolutely impracticable. One of the possible solutions for off-peak utilization appears to be in the adoption of some system where fuel is also utilized and the radiation losses are not excessive under conditions of banked fire when the electric portion of the heat energy is not in use. Some of these combination processes may promise a solution of the off-peak load situation more attractive than the straight electric furnace, which is difficult to cool down entirely without unduly affecting the conditions. In all plants the volume of output is the determining factor in absorbing the general overhead charges, and any intermittance must diminish output with its accompanying disadvantages.

If the furnace could be operated on the off-season load and its product stored, and the chemical works utilizing this product could operate on a normal schedule, this would form one solution; or another would be, if by chance the off-season power were available at the time the greatest demands were to be met, such as preparing a fertilizer product at the season of fall rains for the early spring delivery. All of these plans, however, suggest the necessity of operating at least a portion of the plant continuously in order to meet fixed charges and preserve an operating organization. If the chemical works require a moderate amount of power for its processes in year-around operation and only its surplus for manufacturing its crude material at the off-season peak, it promises the greatest possibilities.

The future of nitrogen fixation is alluring and promises many developments along lines other than those we have considered, but already the market has felt the effects of these various processes, and instead of nitrogen being figured at thirteen cents per pound, it is confidently predicted it will very shortly find its level at a selling price of about eight cents, making a cost of production of five to six cents per pound and thus reducing

sodium nitrate to about 1.33 cents per pound, or approximately $30 per long ton, and the lower-grade mines will feel this and be forced to curtail.

It therefore seems very certain that before twenty-five years shall have elapsed since Sir Wm. Crookes made his memorable address, the Chile nitrate beds will have vastly curtailed their production, not from exhaustion, but from the inroads made by the onward advance of chemical and electrochemical engineering.

DISCUSSION.

C. W. Bennett (*Communicated*): This paper is interesting from the standpoint of the fact that it presents practically nothing that has not been published. A review of nitrogen fixation processes has been published in these Transactions.[1] The Serpek process has been discussed,[2] and the Haber[3] process has been described in other journals. If the gentleman had taken the cost of by-product ammonia and said that nitrogen fixation processes must fix nitrogen at approximately that cost, the final result would have been obtained at once. It seems to me that the situation is this. By-product ammonia will fix the cost of nitrogen fixation processes. No process at the present time measures up to that figure, and therefore, it would appear that no process in operation is commercial. This statement was made by me in a discussion before the Pittsburgh Section of the American Chemical Society about a year ago. It seems that it is borne out by the facts presented in these papers on nitrogen fixation.

L. L. Summers: I think the criticisms of my paper by Mr. Bennett, which the Secretary read, are based on lack of knowledge. There are several points raised, and they all relate to each other. Regarding the relation of nitrogen and oxygen, the Haber tables show what combination would be obtained when there is 50 percent nitrogen and 50 percent oxygen, also various other ratios, but in practice the dissociation due to the tempera-

[1] Trans. Am. Electrochem. Soc., **6**, II, 17 (1904); **16**, 131 (1909).
[2] Trans. Am. Electrochem. Soc., **23** 351 (1913).
[3] Met. Chem. Eng., **11**, 211 (1913).

ture at which you are working does not justify the expense of preparing an atmosphere higher in oxygen content.

Lord Raleigh was the first to point out this advantage, and he made extensive laboratory experiments to prove that the results were possible, but commercially they have not been realized; likewise the maximum temperature of the arc has not been realized, as the temperature of dissociation really determines the commercial concentration. You could get greater concentration if you would raise the temperature, but dissociation would be increased, so that a compromise is effected which gives the best yield per kilowatt hour, and the furnaces are being operated on that principle.

As to the question of the competition of a natural product, a well-known question is: "What is a ton of coal worth in the Desert of Sahara?" There are several gentlemen still in the Desert of Sahara speculating on what a ton of coal is worth. The largest natural deposits of phosphate rock are in this country. We have vast deposits of low-grade rock running from ten percent to eighteen or twenty percent that would be of inestimable value if they could be concentrated or used closely adjacent to where they are situated. There is no acid to make the superphosphate, and no simple way of utilizing it. What is the phosphate rock worth under these conditions?

It is often the same with the coke oven; you have ammonia, but there is no means of placing the ammonia on the market. For years and years great quantities of ammonia liquors ran to waste, and it was not until organizations were provided by which they could take ammonia liquor or sulphuric acid and transport these to the place of manufacture, that ammonium sulphate processes were brought to the point where they competed with Chile nitrate.

Arguments such as those of Mr. Washburn and Dr. Peacock refer to the waste there is in American commercial methods. Freight rates are high, not as high as they are abroad, but distances are greater, so that the freight rates in this country are prohibitive on this class of product. If you had some means of using the phosphate rock in Tennessee, in Wyoming or in Florida, without transporting it to some place where a by-product

is available to make the available phosphate, the phosphates would be cheaper and we could get more farmers in this country to use them. There is no means of rotating crops to produce phosphate as there is for producing nitrogen. The problem is of such importance that our higher grades of phosphate rock leave Florida and go to Germany and Belgium and Holland, where they are manufactured into mixed fertilizers, sent back to this country and sold within a few miles of the place they came from. It is simply a question of commercialism.

L. H. Baekeland: I believe very much with Mr. Summers that the development of nitrogen industries in this country, or the consumption of nitrogen or other fertilizers is a question of opportunity. I happen to be pretty well acquainted with conditions of the utilization of fertilizers in Belgium. It may interest you to know that Belgium uses considerably more nitrogen fertilizer than Germany, and that the yield per acre in Belgium, especially in Flanders, is decidedly higher than the yield per acre of any other country.

Belgium does not use nitrogen fertilizer for the sake of making the nitrogen industry grow. Belgium has been compelled to do so. It has been a process of gradual development. In Belgium the rents of land are very high, abnormally high. In Belgium, like in practically all European countries, the main laws, for thousands of years, have been made by land owners. The most respectable kind of property consists of land estates, and the landlord legislators have given the poor tenant the limit. The result is that in Belgium, like in other countries in Europe, the rents of land in many cases are decidedly higher than what we can purchase land for in this country, and the tenant has to pay most of the taxes beside. Furthermore wages for agricultural labor are very low. If you consult the statistics of farm-labor wages in Europe, you are apt to be misled, because the main labor that counts is the labor which the family of the farmer performs. The tilling of the soil is a family affair in which women and children participate; the cost of their labor is practically what it requires to keep them alive, and they live in an incomparably more frugal way than our farm laborers. This combination of factors makes it necessary for farmers to

practice intensive culture of the soil, and to use fertilizers in order that they may be able to get enough out of their land so as to be able to pay their heavy rents to the landlord, and this more than anything else has developed the fertilizer industry in Europe.

We have heard the statement that in many cases it is more expensive to buy fertilizer than to have a low yield per acre. This is very true, and if the price of fertilizer gets too high, a low yield per acre becomes practically unavoidable. Unfortunately, in this country we are almost everywhere confronted with the detrimental economic condition of too many middle men, and the great difficulty of delivering an article from the manufacturer directly into the hands of the consumer. There used to exist the same state of affairs in Belgium. I remember as a boy, in Flanders, how some very respectable people became tremendously rich by buying guano and putting dirt and sand into it until it still smelled somewhat like guano, and then they sold it for guano to the ignorant and helpless farmers.

In this way the poor Flemish farmers paid dearly for the very lowest grade of fertilizers; but after a while they became wiser and as a matter of self-protection they started co-operative societies among themselves for purchasing of their fertilizer and other farm supplies under more favorable conditions, and I do not think there is now any country where fertilizers can be purchased as inexpensively, delivered directly to the consumer, guaranteed not only by the manufacturer, but guaranteed by the chemists, or analysis of the co-operative societies, as in Belgium. That is the reason why the consumption of nitrogen fertilizers in Belgium has taken such a rapid forward stride.

I truly believe that the time will come in this country when there will be a more direct distribution from the manufacturers to the consumers and a resulting lowering of prices and the consumption of fertilizers is then bound to increase rapidly; from that time on the conditions will be very similar to those in Europe. You will then no longer speak about an excess of ammonia production in gas or coke ovens. There will not be such a thing as excess of ammonia. All ammonia will then be saved. The price of ammonia will then be regulated by the con-

sumption and other conditions which I have mentioned, rent and labor, and the market price of the farm product.

W. R. Mott: Five or six years ago I went over the literature of the nitrogen fixation processes and worked out an equation of efficiency that applied to any nearly stationary arc process. I never published it, but I think it is of sufficient interest to place on the board and to enlarge on a few of the fundamental principles for a good electrical process.

The first principle of efficient operation is to very rapidly cool highly-heated air. For one thing, this means using small arc cross sections. I have deduced from both theoretical and experimental data the following equations for the efficiency of yield for arcs of different current. Let R represent grams of nitric acid produced per kilowatt-hour.

$$R = \frac{K_1 \sqrt{C - K_3} + K_2}{C}$$

Let C represent the arc current in amperes. Let K_1 equal 5.24; K_2 equal 1.25; K_3 equal probably 0.001. The equation is consistent with certain theoretical considerations that I could not possibly enlarge on at the present time. Now, if the current is very large, in this equation, you perceive that the value of the efficiency falls off to a very low degree. The result is that as you reduce the current the efficiency increases. The constants that I worked out were such that the maximum efficiency came at about 0.001 to 0.002 ampere. The constant K_3 is not very accurate, but it is probably not far from the value 0.001.

The smaller the current the greater is the efficiency up to a certain limit, which is probably that of a current of the order of magnitude of 0.001 to 0.002 ampere. Commercially, the smaller the arc the more bulky and costly must be the apparatus for unit power using the same. Also the cost of regulation per unit power increases enormously. Merely these two facts would have been sufficient to have made the process of Bradley and Lovejoy impractical.

The first principle of very rapidly cooling the heated gases

can also be secured by using rapidly-moving air currents, rapidly-moving arcs, and by using sprays of cold material. The success of the process of Birkeland-Eyde over other processes lies chiefly in the small bulk of apparatus required per unit power. A greatly increased concentration results, with a given apparatus. The possibilities of increasing efficiencies of new apparatus are very great.

The second principle is to use the heated gases leaving the arc to heat the cold gases entering the arc. This is most important and will probably lead undoubtedly to great improvement in the efficiency of the commercial manufacture of nitric acid from the air. In order to secure the equivalent of current change you must get the cooling effect by some other way, cause it to sweep through the air, or do the equivalent thing of causing the electric current to sweep through the current of air very rapidly, as in the Birkeland-Eyde process.

The third principle is catalytic, and the fourth increased oxygen. As to the fifth principle, I should say that the apparatus should be designed to work safely and conveniently under great pressure. The sixth principle is that the apparatus should be made of cheap, durable material, that will resist nitric acid and great heat.

In the last place, I would say that efficient means of regulating the electrical energy must be designed.

These principles represent a great variety of possibilities. I do not think they have begun to be used to any extent, in spite of all the patent literature and research work that has been done. Millions of dollars have been spent in research work in connection with this subject.

Francis C. Frary: I am sorry to see so many able mathematicians pass by Mr. Mott's equation. He said that if the current becomes zero the value of the efficiency becomes zero, whereas it evidently becomes infinity.

Jos. W. Richards: The quantity C occurs also in the numerator, and the value of the radical will become imaginary before C gets to zero.

W. R. Mott: Relative to this equation, I am glad Dr. Frary

has called my attention to the misstatement. The curve of this equation gives the following values:

Amperes in arc or spark	Grams of HNO_3 per kilowatt hour
10.	1.8
1.	6.45
0.5	9.0
0.3	13.7
0.1	29.
0.05	47.
0.01	177.

When C is smaller than K_3, then the equation reads, $\sqrt{-1}$ times infinity plus infinity and the physical significance of such an equation is unknown.

W. S. Franklin: I was talking to my brother, an ammonia chemist, a year or two ago, about some of his work on ammonia acids, bases and salts, and about some of the remarkable reactions which take place in liquid ammonia. I asked him what he thought of the possibility of finding a spontaneous combination of nitrogen with some of the metals, say, like calcium or magnesium in the presence of liquid ammonia, which would correspond exactly to the spontaneous combination of the oxygen of the air with iron in the presence of water, and he expressed himself as thinking that perhaps there might very probably be such a spontaneous reaction.

If we lived in a perfectly dry world in which there was no H_2O, we would be up against the problem of fixing atmospheric oxygen. I doubt whether there would be any spontaneous process of oxidation that we could make use of. We might have to resort to the electric furnace in order to reach temperatures high enough to make spontaneous oxidation possible in the absence of water.

Now, fortunately, we live in a world where free ammonia is below, perhaps, one-millionth of a percent in the atmosphere, so that liquid does not normally rain down on us as we walk around. If we put a piece of magnesium or aluminum out in the air, it does not become wetted with liquid ammonia, and nitrified. It seems to me likely that a reaction might be found which could be carried on in a large iron tank in the presence of liquid ammonia and free nitrogen, in which the combination of the nitrogen

with the metal would take place spontaneously at a rate which would make it a commercial process for nitrogen fixation. This is one thing which ought by all means to be investigated.

F. C. FRARY: In regard to the relative price of ammonia and cyanamid nitrogen, the last speaker indicated that the total production of nitrogen in the form of cyanamid and ammonia was less than ten percent of the world's consumption of nitrogen; the ratio being something like several hundred thousand tons to several million tons. I understand that the world's consumption of Chile saltpeter is going up by leaps and bounds. It is generally considered that the price of nitrogen is fixed by the cost of Chile saltpeter, and not by the cost of ammonium sulphate.

In regard to making magnesium and calcium nitride, I would say there would be no difficulty at all in getting the elements to combine. We can make them do that at ordinary temperature.

W. S. FRANKLIN: I wish to be taken seriously in what I said, Prof. Frary (in a conversation between himself and myself) rather took exception to it, from the fact that the materials I mentioned were rather expensive. I did not mean to limit the suggestion of the possibility of spontaneous combination of nitrogen with any particular metal such as magnesium or aluminum. There may be for example a spontaneous combination of nitrogen and iron in the presence of liquid ammonia.

FRANCIS C. FRARY: The point I meant to raise is that the materials which are most active and are capable of combining with nitrogen directly are, like calcium and magnesium (which do this most rapidly), the ones which are the most difficult to prepare.

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THE CYANAMID PROCESS.

By Frank S. Washburn.

The fixation of atmospheric nitrogen has had commercial application for the past ten years. During this period different types of processes have been conceived; four, the Serpek, Haber, Arc and Cyanamid, have seriously attempted commercial exploitation; two, the "Arc" and "Cyanamid" processes, have proved to be commercially practicable in the broad sense. Of these two the latter may justly claim to be of great economic importance to the world because the unit of fixed nitrogen in its first product is capable of being more cheaply produced than by any other present-known process, and because this first product has a direct and valuable use of itself and constitutes the raw material for a varied and important line of derivatives into which, for the most part, it can be cheaply transformed.

The annual productive capacity of the existing plants employing the "Arc" and "Cyanamid" processes is between 90,000 and 100,000 net tons of fixed nitrogen, which, at the normal average value of the product at the factory door, represents $25,000,000. This total quantity of fixed nitrogen is divided in the ratio of two-thirds to "Cyanamid" and one-third to the "Arc" process. The American Cyanamid Company's factory at Niagara Falls, Canada, has alone a capacity in fixed nitrogen approximately half as great as the total world's installed capacity by the "Arc" processes.

More than three thousand technical articles dealing with almost every conceivable phase of nitrogen fixation have appeared in different languages. The patents applying to the subject in all its branches number into the thousands. So far as the author of this paper knows, nothing has appeared in the nature of a differentiation of processes based on the economics of the world demand for nitrogen. It is only for a limited developmental

period that the theoretical, technical advantages and limitations of related processes constitute a practical basis for hazarding opinions as to their ultimate commercial value. It is also true that until an art has had some years of commercial application it is impossible to analyze and draw sound conclusions from the economics of the situation, the final arbiter in determining the social value of any process.

The art of atmospheric nitrogen fixation is now old enough to enable one to see the economic aspects of the case, and therefore, in casting about to determine what part of this vast subject to deal with in this paper, the author thought it would be of interest and possibly of value to treat herein the broad commercial outlook for the various fixation processes, and in order to limit the matter to conditions more or less well known to all of us, conditions on the North American continent, for the most part, will be the only ones considered.

Two nitrogenous compounds, nitrate of soda and sulphate of ammonia, constitute in value 80 to 85 percent of the total raw nitrogen compounds produced throughout the world. The value of their combined production in 1913 was between $190,000,000 and $200,000,000. It is estimated that 80 percent went to agriculture, corresponding to an annual per capita tax on the 600,000,000 inhabitants of the earth of thirty-three cents.

Nitrogen has four main uses: as an agricultural fertilizer, as nitric acid and derivatives therefrom, as ammonia, and in dyes and various other chemical compounds. Measured in the quantity of contained nitrogen, and in view of the restricted opportunities in the United States for immediately developing the chemical and dye industries on a large scale, we need consider as bearing decisively on atmospheric nitrogen fixation processes only the three first-mentioned uses, namely, for crop fertilizer, for nitric acid and its derivatives, and for ammonia as such.

The farmers' purchases in nitrogen used east of the Mississippi River last year approximated $75,000,0000. More than 90 percent of fertilizer nitrogen is in the form of ammonia. The normal annual consumption of nitric acid in the same region is about $7,000,000. The price paid per unit of nitrogen is about the same for each, and the percentage annual increment of consumption is about 10 percent in each case. However, the im-

portance of the fertilizer field in comparison with the nitric acid field, in their bearing on the fixation of atmospheric nitrogen, is not fully nor even approximately measured by this ratio of ten to one.

The use of nitric acid is along established lines looking comfortably to the future for a steady growth, with no serious limitations hampering modest development and no great unsatisfied human need demanding great development. It is essentially a small business as great industries go. The fertilizer industry has a very different significance. The population of the United States from 1900 to 1910 grew from 76,000,000 to 92,000,000, an increase of 21 percent. Crop production increased 10 percent in the same period. Exports of wheat and flour decreased from 31 percent of their production to 13 percent. The importation of foodstuffs and live animals practically doubled, while imported manufactured foodstuffs more than doubled. Beef cattle production fell off 32 percent as the population increased 21 percent. These figures are strikingly reflected in the increased cost of foodstuffs, which from 1896 to 1912 amounted to 80 percent in the United States, while the general advancement in the cost of living during this period was 59 percent in the United States, 40 percent in England, and 40 to 45 percent in continental Europe.

These facts point to the necessity of increasing crop yields without additional labor—and that defines fertilizer. European yields per acre cultivated are 50 to 100 percent greater than American yields. The use of fertilizer in Europe, per acre cultivated, is enormously greater than in America. The average increase in yield in Germany for the past twenty years has been approximately 60 percent, in the United States 20 percent. Abroad this increase is attributed to intensive farming, better selection of seed, the rotation of crops and, to the extent of 50 to 70 percent of the increase, to the use of commercial fertilizers.

The farmers' purchases of fertilizer in the United States last year in nitrogen and phosphorus constituents (later it will be shown why both are here included) was approximately $150,000,000. Were the cultivated lands east of the Mississippi to receive for each of two years out of every three the quantity of

fertilizer normally used per acre each year in Germany, the bill would have been approximately $1,600,000,000, or ten times as great as the actual expenditure. The very limited use of fertilizers in the United States does not arise from the possibility that fertilizers do not pay. Indiana experiments, conducted in ten counties, produced an average increase of 11.6 bushels of wheat per acre, valued at $11.60, for an expenditure of $3.67. An instance of a very low return in the use of fertilizers is an unpublished record of thirty-seven experiments in Illinois in 1913, showing an average increase of 5.2 bushels of wheat, valued at double what the fertilizer cost.

The fertilizer industry today suffers many handicaps. These originate in part from the farmer's limited capital for properly conducting his business, his lack of knowledge which closes to him what would otherwise be avenues of advancement and prosperity, and in part also from the fact that there is no vital, broadcast propaganda and educational bureau conducted by the fertilizer industry.

The greatest handicap is possibly in the material used. The industry is carried on by collecting at a great number of places throughout the agricultural regions east of the Mississippi a great variety of materials, each containing some one of the so-called plant foods, namely, nitrogen, phosphorus and potash, the last representing only about 10 percent of the total. For the most part these materials are low in fertilizing value, and when mixed in a manner to include the cheap as well as the high-priced materials, there results of necessity a product of which 85 to 90 percent is useless dead weight, only the small remainder having fertilizer value. Forty percent of the annual fertilizer product in value is in the nitrogen constituent drawn from materials that are either by-products or wastes, such as sulphate of ammonia, slaughter-house refuse, fish scrap, vegetable refuse, waste of sugar works and distilleries, hair, leather, wool, hoofs and horns. The phosphoric acid constituent is secured from acid phosphate analyzing from 14 to 16 percent P_2O_5, and as a general rule constituting one-half of the complete fertilizer mixture. Few of these raw materials in the broad sense are satisfactory. They are borne with because up to the present time there are no others commercially available. They pay the uttermost limit

in the way of transportation charges to the point of their preparation, and after being mixed they bear a further great transportation burden to the consumer's railway station. There is a relatively large expense for mixing, storing, drying, bagging and selling. After the farmer has received his goods at the railway station, he must haul over spring roads, often almost impassable, 1,000 pounds of material in order to get 150 pounds of plant food. It is one of the recognized, recurring, contributing causes for small crops, particularly in the South, that the roads are so bad in the spring, due to rains, that farmers cannot haul the necessary amount of fertilizer.

Notwithstanding the consumer pays for a variety of materials, a price greater than their quantity value, the fertilizer industry as a whole, which prepares and sells the product, is conducted without measurable profit.

Unless revolutionary developments in some vital respect come to the aid of this great industry in the United States, any marked improvement is impracticable. It would appear, for reasons already set forth, that possibly the matter of greatest economic importance in the United States today is that conditions shall be brought about by which the farmer will use a vastly greater quantity of fertilizer than is now used. We believe the most important single contribution to this end would be a high-grade chemical salt containing nitrogen and phosphorus, well balanced and in large percentages, and possessing in a high degree the many requisites of a good fertilizer, such as being non-hygroscopic, non-toxic, finely granular in form, non-leachable in the soil and readily convertible by nature's forces into the organism of the plant. The process for the fixation of atmospheric nitrogen that will contribute the nitrogen content to such a fertilizer compound to the greatest net advantage may be justly viewed as the most important, not only to society, but also therefore to those who exploit it.

Discussions of the ultimate commercial superiority of a favorite process and the assumed complete annihilation of every other have been almost interminable. These have proceeded apart from any broad conception of time, place, the demands of mankind or the quantitative application of the product. They generally take the form of rival claims for cheapness in the

cost of production, without much reference as to whether the unit cost applied to a form of nitrogen for which there was any particular or large demand, and without reference to whether the product was to be produced at a place and in a form enabling it to be transported to the consumer.

The Serpek process was discussed by volunteer adherents without knowledge that per unit of nitrogen fixed the necessary expenditure of heat energy from electricity alone is as great as the total electric energy consumption in cyanamid. Therefore, no suspicion was aroused that possibly nature had not placed the necessary raw material, bauxite, within practicable shipping distance of equally necessary cheap water powers. The limitations of the by-product, upon which the commercial possibilities of the process depend, were not questioned either as to the difficulties in converting it to commercial aluminum or as to the relation of its volume to the market demand for the metal.

The Haber process has been taken by the public for granted as one practicable of universal application because of its large though single use by a great concern of brilliant accomplishments in the commercial chemical world. The public does not know of the pressing problem of disposing of great quantities of sulphuric acid, and the single problem involved of how, under the peculiar local conditions of cheaply attainable hydrogen and nitrogen, to devise the cheapest possible means of providing the requisite ammonia for using the acid in sulphate of ammonia. The electric energy necessary to the process is generally considered negligible, and yet a proposal to establish a plant close to New York involved, at the necessary power cost in that vicinity, as great an expense for electric power as the total power cost for cyanamid in an available site then under consideration for that process.

Air nitrogen fixation processes divide themselves into two broad classes, namely, those that come in at the nitric acid end, and those that come in at the other extreme, the ammonia end. There is no expectation that the various "arc" processes producing nitric acid will ever have employment in the production of ammonia compounds, for the sufficient reason that there is no prospect of ever being able to commercially convert nitric acid to ammonia. Therefore, the best that can be said of the

"arc" processes is that they may be able, by reason of having nitric acid as their first product, to occupy exclusively the field for the production of nitric acid. We have already seen that this field is not only relatively but absolutely a limited one for the present, as it is prospectively for the future.

The "ammonia" processes are not ready to admit, however, that there is an insurmountable barrier separating them from the nitric acid field. A tried, thoroughly workable, commercial plant for the oxidation of ammonia into nitric acid is not yet complete and in entirely satisfactory operation, but, on the other hand, the various steps necessary to the operation of such a plant have been separately brought to such stages of development as to leave no doubt in the minds of the experienced men who have worked upon the problem of the ultimate complete commercial practicability of carrying the ammonia processes for the fixation of atmospheric nitrogen through to the nitric acid producing stage.

A powerful factor operating as a disadvantage in the "arc" processes to the manufacture of nitric acid is the extraordinary difficulty of transporting the acid from the remote, cheaply developed water powers, very limited in number, where alone these processes can be employed, to the place of use for the acid, both sea and rail transportation being practically invariably necessary. This audience does not need to be told how serious a matter is this. The nitrate compounds made from acid produced by the "arc" processes have found no place as a fertilizer in this country. Nitrate of lime, even in the so-called basic form, is too strongly hygroscopic to permit its use alone or as part of a mixture to be used through the ordinary drills by which fertilizer is distributed to the soil in this country. Even if the physical form were entirely satisfactory, it could not properly have a very large place in fertilizer mixtures in this country because of its being too readily available in the soil and because the valuable form of fertilizer nitrogen is as ammonia and not as nitrate. We have seen furthermore that the fertilizer industry demands something more than a new nitrogenous material, however meritorious it may be, merely as an additional one to the many which now constitute a part of a complete fertilizer mixture.

For a time it was thought that the treatment of phosphate rock by nitric acid might possibly find a large place in the fertilizer world. Two decisively unfavorable and irremedial results have developed from this attempt; first, the product is excessively hygroscopic, the surface when exposed taking up sufficient moisture to reduce the external parts to a molasses-like condition, and second, the content in plant food, approximately 11 percent nitrogen and 14 percent phosphoric acid, is markedly lower than that readily securable in the new commercial ammonium phosphate compounds resulting from the combining of ammonia and phosphoric acid. When the phosphate is carried to the monocalcic stage, thereby giving it the desired water solubility, the excess acid is of necessity so great that the crop is burned and destroyed. Much money has been spent on these efforts, which have always resulted in failure.

This brings us now to the consideration of the practicability of an ammonia-phosphoric acid compound for agricultural use. The mono-ammonium phosphate, containing theoretically 14.6 percent of ammonia and 61.3 percent of phosphoric acid (P_2O_5) and the di-ammonium phosphate, containing theoretically 21.8 percent of ammonia and 53.4 percent of phosphoric acid, have been recognized by the scientific world for many years as fertilizers of extraordinary value, being in effect perfect materials, as they possess every qualification of a good fertilizer. The manufactured product made in this country has not developed any limitation. Under some circumstances, at least, the results in crop increase are greater per unit of ammonia and phosphoric acid than is securable from any other fertilizer or fertilizer compound, and the question has arisen whether this salt may not produce its result partially from the exercise of the same natural laws that apply to the action of manganese sulphate, for instance, in which there is a crop increase that cannot be attributed to the taking up by the plant of anything contained in the fertilizer. The effect may some day be safely attributed to the inducement that the salt has given to increased activity of the chlorophyl and thereby increased power of assimilation on the part of the plant.

The commercial ammonium phosphate product may be readily produced at will with varying proportions of ammonia and

phosphoric acid, ranging from 13 and 47 to 21 and 46 percent respectively, practically all water soluble. Thus it is that the plant food constituents of this single material, varying between 60 and 67 percent, occupy the entire range of the usually desired relationship between ammonia and phosphoric acid. The phosphoric acid content of the commercial acid phosphate now used in agriculture, a product which, roughly speaking, results from pouring a ton of 52° sulphuric acid on a ton of rock containing 30 to 32 percent P_2O_5, contains from 14 to 16 percent P_2O_5. In value it constitutes about one-half the farmer's fertilizer bill in the United States each year. Whatever advantages a new kind of phosphoric-acid-containing material may have, it should be capable of being produced at a cost no greater than the percent unit cost of phosphoric acid in acid phosphate.

Two methods of manufacturing ammonium phosphate compounds have been developed. One of these is in the proved commercial stage and can produce as cheaply, at least, as by acid phosphate. The other is in the advanced developmental stage and promises still cheaper production costs. The first is applicable wherever cheap sulphuric acid may be had, and the second, which employs the electric furnace in driving off phosphorus from the phosphate rock, is applicable only where there is cheap water power available.

When the problem is referred to the actual conditions existing on the North American continent, the most available process known for providing agriculture in a broad way with the ammonia constituent of an ammonium phosphate compound is the "cyanamid" process. Searching investigation and analysis, for four years, of prospective cyanamid manufacturing sites, covering the United States and Canada, has developed a state of facts establishing the practicability of placing ammonia at the disposal of agriculture and the arts in practically every place of large use in the United States, and cheaper and simpler than could be accomplished in any other way. This may be done by shipment of cyanamid from a central point of manufacture to these various localities and its conversion there into ammonia.

These natural tendencies towards the "Cyanamid" process as the principal source for nitrogen supply might be turned aside, however, unless that material and its important derivatives, nota-

bly ammonia, could be produced and delivered to the consumer more cheaply than by other means and through the employment of capital in such a manner as would induce the investment of money in the undertaking. This brings us then to a consideration of the costs of production applied to a distinctive set of conditions which correspond not only with all the important conditions surrounding the demand for and use of the product but also those which characterize an actual place of production and its geographical relation to the consumer.

There is properly a hesitancy on the part of any business enterprise to disclose actual costs. Such information is frequently made wrong use of, and the risk involved in making it public is wholly out of proportion to the gain. At the same time the author realizes that without volunteering exact statements of comparative cost figures, open to confirmation or refutation, as the case may be, it is difficult to carry conviction to the hearer that one's conclusions are sound. The founders of the American Cyanamid Company have not from the beginning been wedded to any particular process for the fixation of atmospheric nitrogen. The aim and policy has been to conduct the company's activities and research work toward the end of developing a great nitrogen industry. It has investigated many processes with the conviction that it could not hope to have permanent and ultimate success except through the application of the best. Its research work in entirely new fields, and in the regular manufacture of its product, has been practically continuous from the day it first began commercial operations in 1910. It is therefore natural that those connected with the company should feel confident of their judgment on many matters bearing upon the relative merits and limitations of various nitrogen fixation processes.

Therefore, while it may be impolitic to disclose actually attained minimum costs it may be possible to establish particular facts and comparisons which will by their logic carry conviction as to the order of compared processes so far as production costs are concerned, without, however, expressing the exact differences in costs. For instance, by the "arc" process the factory cost of nitrogen in commercial nitric acid, excluding all power costs (derived by applying actual working records to a particu-

lar manufacturing site where all conditions are of the most favorable nature) is greater than the total cost of nitrogen in "cyanamid" including power at $10 per continuous horsepower per annum (at a site where raw materials and labor are relatively high). Furthermore, taking that particular "arc" process which is the lowest in power consumption, the power cost alone, at eight to ten dollars per continuous horsepower per annum in weak nitric acid is greater than the total cost of "cyanamid," including power at the same cost per horsepower per annum (and at a site where raw materials and labor are relatively high). These are actual comparisons and lead conclusively to some irrefutable deductions; first, that the "cyanamid" process can fix nitrogen more cheaply than the cheapest of the "arc" processes, even although a charge of ten dollars per continuous horsepower per annum is made against "cyanamid" and the power is given free to the "arc" process; second, if the cheapest of the "arc" processes, so far as power consumption is concerned, is charged only with power at the rate of eight to ten dollars per continuous horsepower per annum and the process is presented without cost or charge of any sort with all labor, raw materials and supplies, its unit of nitrogen would cost more than the total cost of the unit of nitrogen by the "cyanamid" process. It also follows from these conditions that the total cost of the unit of nitrogen in commercial nitric acid made by the "arc" process cannot by any chance be less than double the total cost of the unit of nitrogen in cyanamid made by the "cyanamid" process. We have seen that the really great application of nitrogen is at the ammonia end and these comparisons are impressive in showing not only that there is no hope of the "arc" process working into ammonia production but also, and what is of more importance, that the "cyanamid" process has to its credit a wide margin of saving in cost to span the gulf between "cyanamid" and nitric acid.

The first step in the derivation of nitric acid from cyanamid is to convert the latter into dry ammonia gas. Such conversion is now conducted in so many places and on so large a scale that the actual cost of the operation, including all losses, is no longer a matter of speculation or approximation. The efficiency has been raised in actual practice to over ninety-nine percent and the

cost, while not negligible, is so low as to add only a small percentage to the ordinary cost of the unit of nitrogen in "cyanamid." Therefore, the facts just set forth as to the cost of the unit of nitrogen in "arc" process nitric acid, compared with the cost of the unit of nitrogen in cyanamid, apply as well to the cost of the unit of nitrogen in pure ammonia gas. Roughly speaking, therefore, there is to the credit of the ammonia, available for oxidizing it to weak nitric acid, fully one-half the cost of weak nitric acid derived by the "arc" process. As a matter of fact the indications are that this span will be bridged by the absorption of not more than one-half this difference, making weak nitric acid by the "cyanamid" process cost approximately three-quarters of the "arc" process. As power is brought below ten dollars per continuous horsepower per annum, production costs by the "arc" processes approach more nearly to costs by the "cyanamid" process. It is possible to make the general statement that the costs per unit of nitrogen in weak nitric acid may be taken as the same for both processes where power costs about $4 per continuous horsepower year.

Comparison of the costs of ammonia gas by the "cyanamid" process and the "Haber" process show, broadly speaking, that the Haber process in its most favorable environment in the United States, involves a cost nearly double that of the "cyanamid" process under favorable conditions practicable of attainment.

It must not be understood that the "cyanamid" process has exhausted the possibilities of further economies in manufacture. As examples, in one new factory study in which the requisite coke is to be made by local by-product ovens, the operations so balance that the fuel gas derived is the quantity required, and as the tar and ammonia products pay for the coking, the coke is had at the price of coal. Where ammonia is derived at the cyanamid factory the sludge from the autoclaves composed of calcium carbonate and carbon may be turned back through the carbid furnaces and maintained in the cycle practically indefinitely as a carrier of nitrogen.

However, the whole story is not involved in a study of production costs, for there are other factors which may have a deciding voice, and of these we may mention as important the

amount of the necessary investment for a given output, the salvage in the case of ultimate abandonment, the ratio of interest charge to the out-of-pocket expense, bearing in mind that the latter may be very much reduced by improved operating means while the former is fixed for all time. Taking the necessary investment in the "arc" process per unit of nitrogen in weak nitric acid as a basis, and assuming power to be placed upon the switchboard at an investment cost of $50 to $75 per horsepower, the corresponding investment in the "cyanamid" process for a unit of nitrogen in weak nitric acid would be about one-half, and as cyanamid or ammonia gas about one-third. It is believed that the Haber process in the United States on the same basis would involve an investment of about two-thirds to three-fourths of the "arc" process. In the contemplation of any enterprise requiring large fixed capital there is a reasonable amount of capital beyond which objections to an increased amount are not to be measured by applying the interest and amortization rate to the estimated costs of production. Converting gold in the bank into bricks and mortar, special machinery and appurtenances, particularly in the application of a new and special art is a serious risk for which there is no exact measure, but which in contemplating the risk should weigh heavily as a guide to judgment.

In the case of ammonia production by the "cyanamid" process the fixed investment may be as low as one and one-half times the annual value of the product and in the case of the Haber process three times. In the case of nitric acid by the "cyanamid" process the investment may be as low as one and one-fourth times the annual value of the product and in the case of the "arc" process with a power investment of $75 per continuous horsepower the fixed investment would be between three and four times the market value of the annual product.

The majority of manufacturing concerns in the United States vary in fixed investment from one to one and one-half times the value of the annual product and the inherent risk in industrial enterprises, for reasonably assured profits demand, for the most part, very special conditions where this proportion is exceeded. Even that class of investments considered most stable as to reliability, permanency and growth, namely, public utility

corporations, do not exceed $4 to $6 investment per dollar gross income. We are therefore met in the case of the Haber and arc processes with the necessity for making an investment which, in the judgment and practice of the industrial world, is wholly out of proportion to the market value of the annual product, while in the case of cyanamid the requirements are within the limits of ordinary commercial practice.

These considerations serve to emphasize the difficulties in commercially advancing any new enterprise. The younger technical men do not encounter these difficulties and therefore do not give them due weight. There is extraordinary difficulty, particularly in the United States, in financing a new chemical enterprise, particularly if it involves a large preliminary expenditure in research and developmental work. The banker's attitude, and properly so, is to compare assets and liabilities. Buildings, equipment and manufacturing sites are acceptable assets notwithstanding that in many companies if the business itself were abandoned there would be little or no value in the physical properties. Knowledge, processes, and ideas are not impressive assets. They are considered in large part to have been something secured at great cost, but, even with good patent protection, practically available for the use of prospective competitors without cost to them. In some other countries such enterprises are viewed quite differently, notably in Germany, where ideas are the foundation of great and profitable enterprises and where by law and practice they are better protected for the exclusive use of those who have developed them than in this country.

The promise, or even the assurance of reasonable profit, is seldom a sufficient inducement to the investor to undertake a pioneer enterprise. The competitive element which dominates almost every other activity is lost sight of by the amateur promoter. He forgets that to the mind of the prospective investor he is in the sharpest kind of competition with those presenting other types and kinds of enterprises demanding capital. His project must grip the imagination with peculiar attractiveness as well as impress the practical sense of those to whom it is brought as not only being prospectively profitable but also assuredly safe with a minimum prospect of loss and a maximum

prospect of profit. Of the many subordinate advantages there may be specifically mentioned an early dividend paying period, a ready market for the securities, their acceptance as good collateral, and a ground-floor prospect in future extensions. In the end it must outweigh, in some cases, literally scores of other projects all claiming equal if not superior merit in every particular. There is another consideration of kindred merit which will be impressive if one considers that in a thing so extensively engaged in as trade in securities, one of the very largest activities in which mankind interests itself, there must grow up inevitably certain more or less arbitrary rules, practices and points of view. These all turn naturally upon the usual thing, and the usual thing is the established industry, or at least an enterprise engaged in an established industry. Therefore, the new thing has a slow and difficult road to travel and its difficulties are more than in direct proportion to the amount of capital demanded. Those fixation processes which employ and own their own water powers make a plea to capital that others cannot make, for the reason that it can generally be shown that should unexpected competitive developments in the remote future drive the undertaking to an unreasonably low return upon the investment, the rental value of the water powers for other purposes will probably insure the continuance of a satisfactory return upon the total investment.

Even if it were granted that the "cyanamid" process is prospectively to play the leading rôle in the fixation of atmospheric nitrogen so far as the most important use of nitrogen is concerned, namely, in agricultural fertilizers, and even if it were further granted that it is the logical source of nitric acid, the question may still be an important one as to whether the raw product of this process may be looked to as the source of a long and important line of nitrogen derivatives. The fact is that there is an almost interminable line of derivatives which can be produced from cyanamid with the greatest technical success and assurance and their manufacture has proved to be in some cases commercially feasible. The direct and valuable application of the raw product, cyanamid, is unique in air nitrogen fixation processes. The proof of this value lies in the fact that fully eighty percent of the entire annual product of normally $15,000,000 value is sold as the raw product.

The principal derivative at the present time is ammonia, which has earlier herein been referred to. None is being made in America at this time outside of the Cyanamid Company's research laboratory, but abroad various plants are producing some fifteen tons of gas per day, part of which goes into high-grade sulphate for fertilizer use and part into anhydrous ammonia. There is also installed and about ready for operation a large Norwegian plant erected for the Birkeland and Eyde interests for transforming some sixty tons of cyanamid per day into ammonia, which will be absorbed in nitric acid for the production of ammonium nitrate. The transformation takes place according to the following reaction:

$$CaCN_2 + 3H_2O = CaCO_3 + 2NH_3$$

This decomposition is accomplished by the use of water and high-pressure steam in autoclaves, and large-scale working plants show an efficiency of over ninety-nine percent nitrogen transformation. The ammonia gas is delivered from the autoclaves mixed with steam and absorbed directly in sulphuric acid without removal of the steam, or passed through a very small ammonia column equipped with condensers and coolers for the removal of the steam, thereby yielding a very high-grade pure ammonia gas. In case it is desired to make anhydrous ammonia it is simply necessary to intensify this drying action and compress the gas; considerable quantities of this ammonia are sold in France in the anhydrous state. The cost of the transformation is almost negligible, as the units have very large capacity and require very little attention.

Cyanamid in the presence of water tends to transform itself slowly to dicyandiamid, and this latter to urea. Methods have been recently evolved which make practicable these transformations either to urea or dicyandiamid with approximately ninety percent efficiency and obtain chemically pure salts as the end product. Dicyandiamid, formula H_2CN_2, contains 66.6 percent nitrogen, or probably the highest concentration of any staple nitrogen compound. It has been proposed for use in explosives, acting as a deterrent, also for use in the dye industry. Its greatest future possibly lies in the ease with which acids transform it into the guanidines, which should find large uses in the

explosive industry. The material has been proposed for use as a fertilizer because of its high nitrogen content, but it is probable that its slow decomposition in the soil will never warrant its use for this purpose.

The United States is importing about $50,000 worth of high-grade urea annually for the celluloid industry alone, and could this material be cheaply produced there is no doubt but that it would find an even greater use in the explosive industry. Considerable quantities of this material have been produced in the research laboratory, which has been tried by the celluloid manufacturers with perfect success. It is now practicable to replace the importations of this expensive salt.

In the field of organic derivatives of cyanamid there is practically no end to the series that have developed abroad. The latest addition to this group has been creatin, which seems to be getting somewhat close to synthetic foods.

The calcium in the calcium cyanamid can be replaced by the heavy metals, and recent experimenting with some very interesting compounds, such as lead cyanamid and copper cyanamid, promise valuable results.

When certain grades of cyanamid are melted with common salt the free graphite in the original material is combined with the calcium cyanamid forming cyanide. A transformation of better than ninety percent nitrogen efficiency is obtained and the resulting product contains approximately twenty-five percent KCN equivalent. This material, which can be prepared so as to deliver it into the hands of the consumer at about two-thirds the present price of high-grade cyanides, requires solution in water and filtration. Both operations are easy, and the filtrate can be used in the place of cyanide for the extraction of precious metals. Large scale experiments have been tried out in various cyanide works throughout the world, and in every case it has proved to be identical in behavior with regular cyanide, showing the same extraction efficiencies. The lower price at which this material can be delivered to the consumer more than takes care of the very simple extra dissolving and filtering operations incident to its use, and there should be, therefore, a very large field for this material supplanting the more expensive, high-grade cyanides.

Naturally when the transformation to cyanide is so simple it is also possible to manufacture ferrocyanide, and enter into the case-hardening field and other uses for this material. As a matter of fact cyanamid itself can be very simply compounded into a case hardener which is the equal of any of the present materials on the market and superior to most of them. The German cyanamid makers have, since the beginning of the war, been swamped with orders for this case-hardening material, sold under the name of "Ferrodur."

Reference has been made heretofore in this paper in a general way to nitric acid production from ammonia. There has been developed recently a new process for oxidizing ammonia to nitric acid at high efficiency. It is believed to do away with all of the limitations of the Ostwald process and, if so, the industry will be in a position to meet nitric acid demands by way of cyanamid at a cost under conditions existing in the United States below anything any other process can offer. The gases leaving the oxidizing chambers are many times more concentrated than those from the "arc" process furnaces and, therefore, condensation is greatly simplified and recovery much increased. The units can be made large or small and their cost is rather low, so that small nitric acid plants can be installed at almost any place in the country within shipping range of the cyanamid plant, it being autoclaved into ammonia and converted into nitric acid at the point of use.

Quite recently the American Cyanamid Company has been using the "cyanamid" process as a means of producing argon gas in quantities, producing the nitrogen by means of the copper process and later eliminating the nitrogen by continued re-absorption in the cyanamid ovens leaving argon as the final gas. Thousands of feet of this gas, highly concentrated, is being sold to the lamp industry, chiefly for American use, but in part to consumers abroad at the home of the chemical industry.

DISCUSSION.

L. L. SUMMERS: The cyanamid process, which I have briefly touched on in my paper and which Mr. Washburn has covered from the general standpoint, originated abroad, and there has been ample time for it to have demonstrated its superiority had it possessed it. Personally, I do not accept the unqualified statement in regard to the success of the cyanamid process that Mr. Washburn puts forth, because while it has been successful I do not think that engineers by any means accept it as the final word in nitrogen fixation.

The tendencies today are unquestionably towards the utilization of combustion processes, that is, utilizing fuel directly rather than electric heat alone. Those developments lead at once into some of the most complex and least investigated fields of physical chemistry. The vapor tension, which Prof. Richards mentioned in connection with calorizing, enters into this subject in a most interesting way and practically controls the temperature. The Serpek process, for instance, was patented to cover a range of temperature from 1,700° to 1,900° C., and no stipulation was made on the partial pressures whatever. As the partial pressure will affect the temperature of this reaction over a range of several hundred degrees, it is evident this temperature limitation is useless. Prof. Richards calls attention to the fact that we know very little of the partial pressures of our materials. We know equally little of the vapor tension and the effects of heating salts of metals, that is, what effect is actually produced.

Last month in lectures before the Royal Institution, Prof. J. J. Thompson gave some interesting results of experiments showing the electrical effects produced on heating salts. In these experiments an electroscope was charged and discharged, and under certain conditions positive electric effects were produced, and under other conditions negative electric effects.

Langmuir has dealt with the question of what takes place when the surface of a substance is reacting, and he has shown that at the outer surface, or fresh surface of contact where two phases come in contact, the greatest activity of reaction takes place. Haber and Nernst had previously shown that velocity of reaction is, after all, a fundamental measure of the chemical

force, and at this surface of contact where minute distances were dealt with, and particularly at very low pressures, very marked action of the atoms is noted.

This question, then, of the effect at the contact surfaces, whether it is electrical, or how it is affected by the partial pressure, comes very actively into the question of nitrogen fixation, and at a partial pressure of about one-half atmosphere the temperature of the nitrogen reaction is greatly lowered. The deterioration of the retorts at this temperature, if the products of combustion are separated from the reacting compounds, that is, if the materials reacting are in an enclosed retort, is a matter of serious consideration. If one endeavors to operate with a retort, bringing the compounds in contact with the products of combustion, as in the ordinary blast furnace, then one faces the oxidizing effect of the CO_2 and the CO, and this causes many of the most favorable materials, such as calcium and magnesium, which would form nitrides readily, to form oxides instead.

But today, in spite of these difficulties, this is one of the most promising fields of research.

As to the question of the price of these nitrogen compounds, one is in competition first with the sodium nitrate of Chile, and second with the by-product ammonia of the coke oven and the gas retort. The gas retort had been largely superseded in this country by the water-gas process, but there is now a tendency to return to the retort.

As there is also a large amount of waste heat at the coke ovens, the chances are we will see many of the nitrogen processes operated there for the commercial manufacture of fertilizer.

C. W. Bennett (*Communicatd*): Mr. Washburn has carefully compared nitrogen fixation processes, commercial suscesses and failures, with the cyanamid process, seemingly with the view of interesting capital to invest in this process. No one denies that the preparation of cyanamid is the cheapest working process for the fixation of nitrogen. Nitrogen, from cyanamid, however, is not as cheap as nitrogen from other sources. We must all admit that by-product ammonia can be placed on the market as ammonium sulphate at a profit for very much less, approximately one-fourth the selling price of cyanamid. This industry, as is

pointed out in another communication, is increasing steadily in this country and in others, and it will take the development of only a few other by-products to enormously increase the output of by-product ammonia. If the Pittsburgh district should put in by-product ovens, due to a development of one or more by-products, which seems possible at the present time, the investor can readily see where the price of ammonium sulphate will go. When compared from this standpoint, the manufacturing price of cyanamid must approximate the selling price of by-product ammonia. From this viewpoint, therefore, no process in operation today for the fixation of nitrogen, as has been pointed out a number of times, can hope to compete with by-product ammonia. In drawing conclusions we cannot compare alone the processes for the fixation of nitrogen, but we must also compare the price of the product in question prepared from other sources, because the final user does not care whether his ammonia comes from the distillation of coal or from atmospheric nitrogen.

C. G. Fink: I do not think that the criticism by Mr. Bennett of Mr. Washburn's paper is quite fair. Mr. Bennett says that the ammonium sulphate will be undoubtedly so cheap that the cyanamid process can not compete with it. We usually compare cyanamid with Chile saltpeter. By-product ammonia is as limited as Chile saltpeter.

J. E. Johnson, Jr.: Is the cyanamid plant running or shut down?

C. G. Fink: It is running. I think we should encourage all of these processes and not take the stand of discouraging them, and we should not go on record as doing that.

Jos. W. Richards: Mr. Landis, Chief Technologist of the American Cyanamid Company, has said that his company confidently expects radical changes in nitrogen-fixation processes in the next five or ten years, and that it is prepared, if necessary, to scrap its whole plant inside of twenty years, thinking there might very possibly be no cyanamid process in use at that time.

J. E. Johnson, Jr.: Through the development of the by-product coke oven, that may become true. If any one was to

draw a curve of the rate at which by-product coke was replacing other forms of coke, the curve would run with a very rapidly rising sweep. It is like many other things in this country, when we once make up our minds we do them pretty fast, so the probabilities are that from a starting production of by-product coke a few years ago of five percent of the total it will be fifty percent in a few years. The by-product process is just coming into its own in this country. The process is a success, even if you do not allow anything for the value of ammonia. The process will give a good financial return on the investment and the result is, as we pointed out in one of the written discussions, the price at which oven men are willing to sell their ammonia is going to control the price of ammonia, *per se,* to an increasing extent for a while. But as Dr. Fink said, I do not think that is the final answer. The probabilities seem to be, that in order to get up the production of our farm products to what they are in Europe, we will use many times more fertilizer than we do today and that the use of fertilizer will increase faster than the product of ammonia from by-product ovens.

Turning to the question of the power involved in the production of nitric acid, I wish to ask one or two questions. The speaker before Dr. Fink spoke of the increase in the concentration of oxygen. I have seen the statement in print somewhere that the theoretical efficiency of the process could be raised to something like ten or fifteen times what it is now, by making the concentration of oxygen approximately that of the gas produced by combustion; in other words, doing away with the excess nitrogen. With the processes that have been developed for the production of oxygen in recent years, particularly the distillation from liquid air which they are using for nitrogen at the cyanamid plant, it seems very remarkable that nothing has been done to secure that increased production or increased efficiency of the arc in some of these nitric acid processes. I would like some one to explain why that is. I understand the principal drawback to that process is the tremendous power cost and rather low concentration and rather large apparatus used. Apparently all of these drawbacks are greatly reduced if you use an atmosphere containing something like 50 percent oxygen and 50 percent

nitrogen, or even more, so why is not something being done along that line? There is no doubt about the present success of some of the processes for producing an atmosphere rich in oxygen and it would certainly seem to me to have a tremendous bearing on this situation. I would like to know why more work has not been done in that direction.

L. L. SUMMERS: Mr. Washburn's paper points out that the Birkeland-Eyde people are installing in Norway a cyanamid process for the manufacture of ammonia to mix with free nitric acid, for the production of nitrate of ammonia. When I was at that plant they were receiving all of their ammonia from England in tanks. The question of what the ammonia was worth at the gas house under these circumstances was almost secondary to what it was worth in Norway, being simply a question of the commercial relations of freight rates and transportation to the nitrogen as it existed at the ovens. In England they offer the difference between the cost of producing sulphate at the gas house and the current rate of sulphate, and the material is sold on that basis. It is this commercial point which affects materially the problem of nitrogen fixation in this country. The Birkeland-Eyde process has resulted in the manufacture of nitric acid in Europe, and is the only process by which nitric acid is being commercially made, because the processes which produce it from ammonia, such as the Ostwald contact process, have only been experimental; being unable to get patents in Germany, they have been extremely reluctant about giving any information.

Up to the outbreak of the war there was practically no nitric acid manufactured by any other fixation process than the Norwegian process, and if nitric acid could have been shipped readily (its corrosive tendencies make it difficult to handle) it would probably have been possible to make a larger installation than they have done.

One must feel, therefore, that the production of nitrogen, whether in the form of cyanamid, ammonia or nitric acid, will depend largely on local conditions. We are consuming nitrates at the present time—the world is, at least—faster than we are manufacturing them.

A paper presented at the Twenty-seventh General Meeting of the American Electrochemical Society, at Atlantic City, N. J., April 23, 1915, President F. A. Lidbury in the Chair.

COMMERCIAL NITROGEN FIXATION.

A POLEMICAL NOTE.

By S. Peacock.

Seventeen years ago Sir William Crookes in his presidential address on "The Wheat Problem" to the British Association directed attention to the importance of nitrogen fixation as a factor of economic agriculture, and characterized it as "one of the great discoveries awaiting the ingenuity of chemists." Then, as now, agriculture provided practically the sole commercial justification for the exercise of such ingenuity of chemists; and, for such use, combined atmospheric nitrogen must be prepared to compete with the least costly forms of nitrogen-containing by-products and waste materials. The fertilizer industry of the United States uses annually somewhat more than 100,000 tons of combined nitrogen, computed as ammonia, and the annual increase averages about 8 per cent. The combined nitrogen recovered in the United States from the distillation of coal for various purposes may be stated as approximately 70,000 tons per year, with an annual increase of about 15 percent; and this increase must be assumed to be practicable for several years to come.

As encouragement to commercial nitrogen fixation, it may be stated that many organic nitrogenous substances heretofore used in fertilizers are finding other and more remunerative uses; and with each year a stronger demand is made on sources of supply which must favorably affect nitrogen fixation. A serious limiting factor is the cost. To illustrate: to grow one bushel of wheat requires nearly four pounds of nitrogen, which at present prices on the farm somewhat exceed 60 cents in cost. It is evident that the cost is practically prohibitive.

Agricultural nitrogen hunger has been a practical fact for generations, not because ample nitrogen could not be obtained,

but because it cost too much. Practically, farmers resort to a form of nitrogen fixation by growing leguminous crops in rotation and otherwise, but unfortunately legume nitrogen is scarcely less costly than the commercial product. Commercially, the problem is clear and explicit; either the price of farm products must be materially increased, or the cost of combined nitrogen must be lessened. The former may or may not indicate a confession of incompetency on the part of industrial chemists; it is the problem we have to consider.

As a commercial undertaking, nitrogen fixation must remain substantially dormant so long as the ammonia produced as a by-product of coal distillation remains of such relative amount that it is capable of controlling the rewards of capital invested in nitrogen fixation. It may be accepted as a fact that no nitrogen fixation method has as yet been publicly proposed which can produce combined nitrogen as cheaply as coke by-product ammonia. However, many very promising processes have been suggested, and it is to be hoped that some one or more will prove successful. The paramount objective must be a producing cost at the factory not in excess of four cents per pound of ammonia; such process will lessen the cost of bread and greatly expand the consumption of fertilizer nitrogen.

It is doubtful if any process simply effecting nitrogen fixation will attain the necessary efficiency; it is probably essential to work out a combination process which not only fixes nitrogen, but also accomplishes one or more additional useful reactions. An illustration of such process is the complementary formation of calcium carbonitride and phosphorus nitride, using a mixture of phosphate rock and carbon, with but one heat effect.

With the low cost ammonia, oxidation processes will follow, solving the problem of cheap nitric nitrogen and such compounds as ammonium nitrate. The weak point of American industries generally is the enormous proportion of costs permitted to selling and distribution. Therefore, the concentration of associated values in final end products is an important factor. Thus, ammonium nitrate or ammonium phosphate are more economical than ammonium sulphate, calcium phosphate or sodium nitrate, as the latter carry constituents useless or worse than useless for industrial purposes.

As the fertilizer industry must be regarded as the chief support of nitrogen fixation, the end products must be suitable for fertilizer needs. This implies a product constant in composition, soluble in water, not deliquescent, and one whose component parts do not readily assume undesirable forms, such as a gaseous or insoluble form. It is essential also that, when mixed with other fertilizer materials, such, for instance, as potassium salts, no reactions may occur tending to make the mixture hard and lumpy, or in any way lessen its dry granular state; otherwise the material cannot be used in distributing machines, and thereby becomes practically worthless.

It may be assumed as a governing principle that a commercially successful nitrogen fixation process must give as an end product potassium nitrate, or ammonium nitrate, or primary ammonium phosphate; and, that the factory cost must not materially exceed five cents per pound of combined nitrogen figured as ammonia. It is true that the present price is several times that; but, having in mind the competitive power of by-product ammonia and the vast prospective increase in the production of same, capital is not justified in supporting a nitrogen project under other conditions.

The host of synthetic ammonia processes, of which that of Dr. Haber is the best known example, can never become commercially important, though they may have a moderate local application.

From the point of view of a somewhat intimate acquaintance with all the nitrogen fixation processes publicly known at this time, there is nothing in the above conclusions which should in the least discourage American technologists.

DISCUSSION.

L. L. Summers: I am sorry Mr. Peacock has not gone into some of his work more thoroughly, as he is very modest in presenting his discussion to the public, although he has done some very interesting work. In America we have developed, perhaps, more slowly than they have abroad. They have obtained greater results commercially there, because their conditions are different. In the first place, the water powers of Norway are of such a

nature that the development cost is about one-quarter of our best water power. The largest plant in Norway is most unusually situated, naturally, so that they have been able to apply these processes, due to the very cheap power.

Dr. Peacock's paper is very short and very much to the point. Undoubtedly you all know that Dr. Peacock is one of the best authorities in America on fertilizers—he has been associated with several of the large corporations, not only that, but he has visited nearly all of the European works, and is thoroughly familiar with everything that has been done connected with the use of nitrogen in fertilizers.

Of the problems which he has presented, a great many are of a polemic nature, as it is stated, and the point I wish to raise is that I think improvements will take place that will make it possible to utilize the phosphate rock or utilize the by-product ammonia, nearer to the points of production, and that will give a great advantage over the man who has to transport his raw materials to some central point.

W. R. Whitney: It seems to me that the matter brought up by Dr. Peacock is of the utmost importance to all of us. We are shipping our best phosphate rock abroad. We are selling in this country the cheapest grades of phosphate rock and mixing a lot of diluents with it. We ought to develop our fertilizer industry as highly here as it was developed in Germany and Belgium.

I want to criticize this polemic of Dr. Peacock's, because he has no right to tell us of this Society that such a thing can not be done. It is an unhealthy attitude. An ammonia process like the synthetic process, of which Dr. Haber's is the best known, may well be very successful. They require a catalyzer to make any of them a commercial proposition, and as we know so little about catalyzers, we want to leave the possibilities open to be passed on later on.

I would like to ask for information: if all of the coke was by-product coke and all of the nitrogen in the coke became available as ammonia sulphate, what fraction would that constitute of our present fertilizer consumption of ammonia in fertilizers?

J. E. Johnson, Jr.: I can not give the figures exactly, but in times of normal business in this country there are somewhere

around 45 million tons of coke produced, and there are about 18 pounds of ammonium sulphate, and 10 pounds of ammonia per ton. I am not sure as to the figures, but that is not far out of the way. That would be 450 million pounds of ammonia, which would be about 225,000 tons.

W. R. WHITNEY: What is the percentage of the by-product coke?

J. E. JOHNSON, JR.: I do not think it is up to 30 percent. It has risen from one or two percent up to 25 or 30 percent.

L. L. SUMMERS: There are about 46 million tons of coke made in this country per annum. The by-product coke industry started in 1896 at Glassport, Pa., the second at Everett, Mass.; both were small plants, and the second plant was not making metallurgical coke. The development was very rapid.

As for the figures during the past five years, there is some difficulty in arriving at a correct estimate, on account of the establishment of a plant at Gary, near Chicago, coking 1,000 tons daily in one installation, and four other plants in the vicinity, bringing up the total to 10,000 tons a day, where there were none before. The statistics must be analyzed carefully, and I shall be glad to include some data in the discussion, as I have it in my files.

Another point which would bear investigation is the effect of the temperature to which the coking coal is subject, and that should be made a question for every careful discussion. The coals we have in this country are naturally coking coals, those used mostly in making metallurgical cokes, and the coals in some of the regions abroad are not as good coking coals, and hence a different treatment was utilized abroad than we might have utilized in this country. The result is there is as much controversy today in the coking field as there is in the nitrogen fixation, because when you apply the higher temperature to the coking coal the less gaseous products it contains and the greater amount of hydrogen has a tendency to extract a greater amount of ammonia, but at these high temperatures there is an increased decomposition of the ammonia. The effect also is to destroy the tar products, so that the yield of tar is reduced to one-quarter or one-fifth of what it should be.

The average nitrogen in the coal of this country is about 1.2 percent, which would be equivalent to over 100 pounds of ammonia sulphate per ton. We get in actual practice in good coke ovens today about four pounds of ammonia, equivalent to sixteen pounds of sulphate. Gas-house coke gives about six pounds of ammonia, being equivalent to twenty-four pounds of sulphate. If you pass a large amount of hydrogen through the coke as it is being made, near the final stages, such as decomposing fuel oil with it, you can raise it to fifty pounds. The actual net result is about 40 percent of the nitrogen in the coal remains in the coke.

The effect of passing hydrogen through the coke is that it will yield an increase of ammonia, but there is a difference in ammonia yields of 50 to 100 percent in the different methods of coking in by-product ovens, and there are almost as many different types of by-product ovens as there are processes for fixing nitrogen.

Another question is that of the total nitrogen. Figures differ very radically on the amount of the world's production of nitrogen, that which is used for fertilizer and that which is used in the commercial arts. The best figures would indicate that there are about 3,700,000 tons of saltpeter and ammonia sulphate produced per annum, and one-quarter to one-fifth of that would indicate 700,000 tons of nitrogen. If all the coke was utilized (and we can assume that there are 33,000,000 tons of coke and we get 20 pounds of sulphate per ton) we would have about 600,000 tons of nitrogen, which would lack about 20 percent of being the world's production of nitrogen today.

But the world's production of nitrogen today is not what it will be five years from now, or ten years from now, if you halve the price of it. You have a geometrical ratio and not a straight line function. It is very problematical, and gives rise to great difference of opinion in the interpretation of these statistics, simply because when you change one thing you change several.

Jos. W. Richards: Another large supply of by-product nitrogen, in England particularly, comes from bituminous coal used in gas producers by the Mond process. That has not been mentioned here. There is probably as much bituminous coal used in gas producers as is used for making coke, and all of the nitro-

gen in that case is lost, unless it is saved by the Mond process or one similar to it.

J. E. JOHNSON, JR.: I do not think there is a single installation of that kind in this country.

JOS. W. RICHARDS: In England there is a large output of ammonia from gas producers, and there have also been suggestions made to obtain it from blast furnace gas, but that is a little more remote question.

J. E. JOHNSON, JR.: I think the recovery of ammonia from blast furnace gas, where they use soft coal as in Scotland or the north of England, is carried on commercially. I have no positive information to that effect, but my impression is very strong that it is. As I said, there is no recovery of ammonia from producers in this country, as far as known to me, and I know many of the works where the big producer plants are.

I think Mr. Summers made a slight error in dates in regard to the introduction of the by-product oven in this country. It was started in Syracuse by the Sement-Solvay Company, in 1893. They were the only ones until the Glassport installation, and that was quickly followed by the Dunbar installation.

H. K. HITCHCOCK: There was a producer plant for the recovery of ammonia erected in this country by the Columbia Chemical Co., Barberton, Ohio. Before it was decided to erect this plant, Mr. Galt carefully investigated the operation of these same producers in England and found they were operated successfully there, and giving very excellent commercial results. After these producers were erected here, however, the patentees were not able to operate them with the coal which was used at the Barberton plant so as to get a commercially economical result. Theoretically the process should have been commercially successful, but while it was technically successful, it was never a practical success from an economic point of view.

In this connection there is another possibility for the by-product coke industry which might be interesting. Quite recently I have heard suggestions for utilizing the by-product coke oven to make coke and by-product gases; then pump the gases through existing natural-gas pipe lines in order to deliver the fuel gas at

the point of consumption and at the same time make the by-product coke at the mine where the coal is produced. An arrangement of this kind should be commercially available, and every time the supply of natural gas falls short, and the demand for gas fuel becomes acute, the problem bobs up. I have no doubt it will eventually be done to considerable extent in the Pittsburgh district, and considerable ammonia recovered.

Francis C. Frary: In regard to the statement about by-product ammonia in Chicago and neighborhood, to my personal knowledge the Sement-Solvay Company erected a plant there about nine years ago, which has been continuously producing by-product ammonia ever since.

L. L. Summers: I spoke extemporaneously. I will make one statement. In regard to the Mond process for washing gas, there have been a number of plants tried in this country, but the fundamental weakness is the fact that in washing a low-grade gas, primarily the producer gas is used for combustion purposes, and in gas running from 80 B. t. u. to 140 B. t. u. per cubic foot, which is the range of blast furnace gas and producer gas, you sacrifice its physical temperature, so instead of having a temperature of 1,500, 1,700, or 1,800° F., which you might get direct from the producer (or in the Mond process 1,000° F., on account of the excess of steam used) you sacrifice the sensible heat, and you have reduced the calorific value of the fuel about 18 or 20 percent. To show such a large value of gas requires quite a large plant, and commercially you are on the wrong side of the books.

President Lidbury: It is a fact I might mention that the plants in England are in connection with the engines used for combustion power purposes.

L. L. Summers: The primary installation was laid down by Dr. Ludwig Mond many years ago, in his own works at Newcastle, and that is where the greatest development has taken place.

Jos. W. Richards: The gas was made near the mines and piped to the point of consumption, and therefore the original heat of the gas, in that distribution system, would be lost anyhow.

LEO BAEKELAND: I know there are many important sources of ammonia which have up to this time practically remained untouched. In this country there are immense deposits of peat which, in conjunction with the production of gas, would furnish an enormous supply of ammonia; peat has been utilized successfully for this purpose in some European countries where good coal is less abundant than in the United States.

J. E. JOHNSON, JR.: They tried it in Canada also.

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AN ILLUMINATING ENGINEER'S CONCEPTION OF AN IDEAL LIGHT.

By Herbert E. Ives.

The distinctive function of the illuminating engineer is the ultilization of light sources in the most efficient manner. His criterion of efficiency is that of every engineer, namely, the attainment of the value unity in the ratio of useful work to power consumed. For the denominator of this fraction he uses the same units as the mechanical, electrical or other engineer who deals with purely physical power relations. Into the numerator, however, he finds it necessary to introduce a number of factors —physiological, psychological, aesthetic—which vastly complicate the process of arriving at a high efficiency, or of expressing that efficiency in definite terms.

It is in fact the addition of these non-physical factors that makes illuminating engineering a science or art, or artistic science, apart from the science of light production. The gas or electrical engineer who takes as his problem the production of light is, or at least has been, concerned solely with getting as much light as possible for a given expenditure of power. The form of the light source has not received much attention. The fact that his proudest achievement has usually been a dazzling point of incandescence, with an intrinsic brilliancy so high as to be utterly unsuited for viewing with the unprotected eye, so that it requires a profound modification of form before it is in shape to use, has not, I think, received the thought from him that it deserves.

The light producing engineer turns this presumably efficient light source over to the illuminating engineer. The illuminating engineer proceeds to equip this dazzling point with reflecting, refracting and diffusing auxiliaries until its characteristics are totally altered. He puts it in a deep reflector, so that it is con-

cealed from the worker's eye and so that the greater part of the light is directed where it will be of most use. He surrounds it with a diffusing medium whereby its intrinsic brilliancy or candle power per unit area is reduced by tens or hundreds of times. In the extreme case he spreads the light from this bright point over the whole of the ceiling of a room, so that in place of a light source of a few centimeters area, the actual effective one is to be reckoned in square meters. Thus in place of the harsh black shadows inseparable from the original light source he secures the quality of diffusion. He may also introduce colored absorbing media to alter the quality of the light.

When the illuminating engineer has completed his task he has produced an illumination adequate for the work in hand, not harmful to the eyes and of pleasing character—a truly useful light. The numerator of his efficiency fraction has a high value. But in thus fundamentally transforming the character of the effective light source, the denominator (power consumed) has had to be recklessly increased. Each application of reflector, globe and absorbing medium has taken its toll, until upon the initial criminally low efficiency of light production is piled a burden whose only justification would be sheer necessity.

When the raw materials supplied to a factory are of such a grade that their efficient handling becomes impossible, there are two solutions of the difficulty. One is to make such change in the manufacturing methods that the unsatisfactory material can be used, even if less profitably than it should be; the other is to make such representations to the provider of the raw materials that the quality is improved. Frequently, after consultation between the two interested parties the needs of the one are better understood by the other, and what has been thought an unavoidable characteristic of the material or process of utilization it has been found possible to eliminate.

The thesis I wish to present here is that the illuminating engineer ought to rewrite his specifications. He ought to tell the light production engineer exactly what he wants as a final product. In turn, the light production engineer should be at great pains to acquaint himself with this ideal and keep it constantly in mind as he studies his own specific problems. I have a strong suspicion that possibilities in light production which

would make a great appeal to the illuminating engineer have in the past been overlooked because the investigator has been thinking only of what light sources have been like heretofore, not what they should be now or in the future. I suspect that mere brilliancy has counted for more than real efficiency. Anyone can admire the dazzling intensity of the arc lamp, but it took a real student of the essentials of light production like Langley to realize that the common fire-fly is a much more wonderful light source. Going one step further and in particular illustration of the present thesis, it was a realization of the significance of intrinsic brilliancy, derived from the study of illuminating engineering, that led to the further piece of information about the fire-fly that it makes its light right at the start of that same intensity per unit of surface that we arrive at by elaborate and costly modification processes with our artificial sources. Is it unreasonable to suspect that an investigator, uninformed of the essentials of the ideal light, might readily throw an artificial fire-fly in the junk pile?

The first portion of this paper will be devoted to the presentation of data and considerations intended to give a concrete idea of the kind of light source the illuminating engineer finally produces, but which would more profitably be given him in the first place. Following that, some recently acquired data on the possible efficiencies of light production will be presented. These latter are of interest not only to the illuminating engineer, but to the light production specialist, and are appropriately introduced here because they are obtainable only by combining with physics some of those same physiological points of view which make illuminating engineering distinct from the mere production of light.

I.

THE CHARACTERISTICS OF THE FINAL TRANSFORMED LIGHT SOURCE USED BY THE ILLUMINATING ENGINEER.

Intrinsic Brilliancy: The brightness of the image formed upon the retina is directly proportional to the brightness of the object viewed. What brightnesses are normal and what are harmful? The brightest object by day is a white surface in the sun. Its brightness is about 5 candle power per square centimeter—about

as bright an object as one would care to look at. Its brightness is just about equal to that of the artificial illuminant of lowest intrinsic brilliancy in ordinary use, the Welsbach mantle. Now an ordinary tungsten filament has a brightness no less than 300 times this; the recent nitrogen-filled tungsten lamps as much as 1,000 times. It is sufficiently evident from these figures that, even to avoid injury to the eyes, light sources should be sought with only a small fraction of the intrinsic brilliancy of those now used.

But the illuminating engineer makes even more severe demands in this direction. When, as is commonly the case, he uses the whole ceiling or portions of the side walls as his actual light source, in emulation of the daylight sky, the brightest surfaces drop down to values approximately one one-thousandth of the sunlit white surface, or one ten-thousandth that of the high efficiency tungsten filament.

In order to effect this enormous reduction of effective intrinsic brilliancy it is necessary to employ reflecting or diffusing media, which sacrifice from 30 to 50 percent of the light produced. The demand of the illuminating engineer should be, I think, for a light source possessing intrinsically the characteristics of the low-brightness illuminated ceiling or wall. What he requires is a surface source, of an intrinsic brilliancy not over one one-thousandth candle power per square centimeter. A true luminous paint which could be easily excited at will would meet this idea. Spread upon the ceiling or walls, and using no more of their area than is now requisitioned by the so-called indirect systems of illumination, it would produce their lighting effects at a maximum of efficiency. The enormous difference between the idea of a low brightness surface source and the present high brightness point sources of light is perhaps the most important suggestive contribution illuminating engineering considerations have to offer to the subject of light production.

Visibility, Contrast, Direction: Low intrinsic brilliancy is not alone sufficient for the illuminating engineer. His illuminant must be largely out of sight, and in many cases he puts it at the side instead of overhead. In order to show most quickly how these requirements of concealment and direction may influence

the characteristics of the ideal light let us consider a case of lighting by a window by day. I am not contending that daylight is necessarily best, or that window lighting is better than anything else could be. I want merely to direct your attention to a particular case of window lighting by which certain characteristics of good lighting may be easily illustrated.

This particular case is a side window facing dull opposite houses or foliage. The sky forms the illuminant for the whole lower part of the room; the brightly lighted ground or street below illuminates the ceiling. The eye of the occupant of the room is shielded from direct sight of both bright sky and street by the outlines of the window and its partly drawn shade. This window illumination is particularly pleasing. Let us analyze it.

Analyzed in illuminating engineering terms this window is a case of a light source of large area of low intrinsic brilliancy acting from the side, and of very irregular distribution of brightness. Its most important characteristic is that the effective light source for the greater part of the room, namely the patch of sky of window area, is concealed, at least for the ordinary position of the occupant. It is indeed a general principle of satisfactory illumination, which cannot be here dealt with at length, that the greater part of the useful light should come from a concealed light source in order to avoid undesirable contrasts in the field of view.

Suppose for a moment we take this window as the ideal light source to be copied in an artificial light. To the conception lately mentioned of a luminous paint we must add that it should be applied to the side of the room. And where more appropriately than at the window itself? Why, when we draw the shades, should we not as well draw down the light? The area of wall and ceiling which the illuminating engineer is now demanding to obtain his transformed light source is as great as and is in addition to that already devoted to lighting by the architect. By night our windows are apt to become mere black holes, sacrificers of light. This would be avoided by the luminous window shade to which we have been led by several considerations. Incidentally, those who are electrically minded may picture this shade as traversed by energy supplying wires like an electric heating pad.

The matter of irregular light distribution from this shade is

perhaps beset with some practical difficulties. The "distribution curve" of the window as a light source is unsymmetrical in the extreme. Light is given out only in one hemisphere, a flood of it toward the floor of the room, a large amount toward the ceiling and a minimum directly inward. To copy this without auxiliary apparatus is asking a great deal. But in this connection it is interesting to note that we have actual cases of unsymmetrical light emission. For instance the light emitted from a fluorescent glass surface becomes more and more intense as the angle of emission with respect to the normal increases.

Now, while it is a far cry to the luminous window shade with its peculiarly unsymmetrical distribution of light emission, it nevertheless represents an ideal which should be in the mind of the light production engineer. Let him not carry ever before his mind's eye the picture only of a bright point shedding its rays equally in all directions. If something turns up which will only shine in one hemisphere with a dull glow and which looks differently bright as observed from different directions—do not throw it aside impatiently as a freak. Perhaps the illuminating engineer will hail it with joy!

Color: Most of our ordinary artificial light sources are of a deep yellow color as compared with daylight. They show, when analyzed in the spectroscope, continuous spectra.

The postulation of an ideal with respect to color is not possible because the requirements are different in different cases, but it is this very fact which should be kept in mind whenever anything giving light is found. It will be sufficient here to note two cases of useful color characteristics, namely, daylight color and monochromatic light.

An excellent argument can be made for daylight as the ideal illuminant on the ground that it is the light on which the human race has been reared. Without committing ourselves one way or another on this point it is sufficient to note here that artificial light of daylight color, available at all times, has considerable technical use and that at present it costs excessively. It is ordinarily produced by processes of absorption which use up 80 or 90 percent of the light.

Now there is no intrinsic reason why white light should be

less efficient than yellow; it is in fact the other way about. But even if a white light were found of comparatively low efficiency, the point to remember is this—that its competitor is not the more efficient yellow light, but the only light in its own field, namely, the inefficient absorption product. A natural white light of a third or a fifth the efficiency of ordinary artificial light would have a field all its own. Has such a light lain unnoticed by some experimenter keen only on high efficiency?

The peculiar advantage of monochromatic light, especially green light, is that it reveals fine detail better than does complex light. The draftsman, the proofreader, the loom operator, do best with such light. On the other hand, color values are totally lost under light of but one wave-length. An investigator should have clearly in mind the very different fields for which light is demanded. In discarding as interesting, but of no practical value, a light under which his assistant took on the appearance of a corpse, he might lose the opportunity of proving a benefactor to a goodly fraction of the world's workers.

These two illustrations should indicate how the development of illuminating engineering, or the proper utilization of light, may react profitably on the development of its raw material, namely, light sources, in the matter of color.

II.

THE EFFICIENCY OF LIGHT PRODUCTION.

The question of the efficiency of light production is one which belongs as much to the illuminating engineer as to the light production engineer, partly because it is only possible of evaluation by considering other than purely physical factors, partly because the illuminating engineer meets his most serious limitations in the inherent inefficiency of his light sources.

In illustration of this latter statement let me remind you again of the losses incurred by the use of reflectors, diffusers and other transforming media. But even when the illuminating engineer has done his best in the way of distribution he gives us ordinarily less than one-tenth the illumination which we have come to consider as no more than adequate by day. Verify this in almost any room by drawing the shades at midday and turning

on the artificial light. It is usually almost impossible to believe that the same installation is satisfactory at night. A ten-fold increase in power used for lighting would usually be considered prohibitive yet it is an open question whether this drop in working intensity of illumination is not a cause of eye strain.

It may be stated with some confidence that the illuminating engineer can now provide any lighting effect desired if he is given a deep enough purse. He can analyze the effect to be copied, and copy the essential elements by combinations of his bright lights and his diffusing media, but the process is very costly. Thus to reproduce the window illumination discussed above, the copy having both the intensity and color of daylight would have cost, as found by experiment, the expenditure of twenty kilowatts, instead of the fifty watts normally allowed for the room! Now, it is capable of demonstration that if light production were pushed to its ideal efficiency fifty watts would have sufficed for the complete high intensity daylight copy. From this it is evident that the illuminating engineer's hands are tied until he is given light sources of high efficiency. The striking comparative figures just given anticipate as well the results of the next paragraphs. These show that the illuminating engineer ought to have, and in the course of time probably will have, light sources of an efficiency which will cause these days of Great White Ways to be regarded as the Dark Ages of light production.

The efficiency of any machine is properly measured by the ratio of useful work to power consumed, each being measured in the same units. Put differently the efficiency is the ratio of the useful work actually done to the greatest possible amount of useful work that could be done by the amount of power consumed. To measure efficiency we must, therefore, either express input and output in the same units or else know the maximum possible value of the ratio in such different units as are in use.

In the case of light production the power consumed and the light produced are commonly measured in different units; the power in watts, the light in lumens, the lumen being a unit derived from the dimensions of some long forgotten candle. At the same time the maximum possible efficiency in lumens per watt has not been known. As a consequence there has been

absolutely no way to tell, except in the crudest possible way, whether an illuminant is an efficient light producer or a thing to be ashamed of.

Several researches recently completed have aimed to better this deficiency in the science of light measurement. We have developed methods for measuring the luminous efficiency of radiated power on a logical scale, namely, that on which the most efficient radiation (in the yellow-green of the spectrum) has an efficiency of unity or 100 percent. We have as well made a determination of the lumens per watt of the most efficient radiation, by measuring both as light and power monochromatic green radiation. The objects of this latter measurement were several; one was to pave the way for the adoption of the watt as the unit of luminous flux, but the use we will make of it here is to learn how far our present illuminants fall below what should be possible.

In the following table are shown on a rational scale luminous efficiencies of the radiated power and the total efficiencies of some representative modern illuminants, the difference between the two figures showing the applied power lost in being transformed into radiation.

Illuminant	Luminous Efficiency of the Radiation	Total Luminous Efficiency
Standard "4-watt" carbon lamp	0.0045	0.0042
Vacuum tungsten lamp 1.25 w. p. c.	0.0165	0.013
Type "C" Mazda 0.7 w. p. c.	0.0293	0.024
Welsbach mantle 0.75 percent ceria	0.012	0.0019
Open flame gas burner	0.0019	0.00036
Yellow flame arc	.....	0.072

There is one comment on these figures that cries aloud. The efficiencies of light production are appallingly low! If in addition to these figures we take into account the low efficiency of utilization of the energy in the most widely used source of power, namely, coal, we are face to face with the fact that at the present time one percent is about the top figure for the over-all efficiency of light production. In the face of such figures, solicitude for what is lost in the smoke of our chimneys seems misplaced. Light is actually only a by-product.

Obviously if the illuminating engineer had at his disposal light sources reasonably approaching full efficiency, say as nearly as

an electrical transformer does, he could shake off many of his limitations. It is of interest to inquire along what lines we may expect the attainment of these efficiencies which are theoretically known to be possible.

The most common way of producing light is by heating matter to incandescence. Straight temperature radiation, as it is called, has probably—but one must avoid dogmatic statement, which is always rash—been pushed about as far as it can be on the earth. If we could produce solar temperatures and handle matter at these temperatures we could look for substantial increases in efficiency by temperature radiation.

Another method of light production is by selective high temperature radiation, which is exemplified by the Welsbach mantle. Certain substances, notably the oxides of the rare earths, are unequally transparent in different parts of the spectrum. Therefore, in consequence of Kirchhof's law they emit radiation unequally when heated. In the Welsbach mantle there is a long strip of transparency in the infra-red. This has low emissive power, while the visible portion has high emissive power, a set of conditions resulting in high luminous efficiency. The exact results of combining all the various oxides and other available substances have never been scientifically worked out. Along these lines it is reasonable to expect marked advances.

The last method of production to be considered is by luminescence or non-temperature radiation, a term used to cover fluorescence, phosphorescence, organic light production, the production of light by chemical combination and the like. These forms of light production are in general characterized by low intrinsic brilliancy. They have probably for that reason received little serious consideration as forms of practical illumination. Yet that most efficient known light source, the fire-fly, is of this type.

It is at this point that we may profitably return to the demands, other than for efficiency, made by the illuminating engineer. He has been represented as making a protest against the concentrated point source lights of the present as being unavailable in their natural form for his purposes. He asks for sources of low intrinsic brilliancy. May it not be possible that in these luminescent phenomena will be found the answer to all the de-

mands of the illuminating engineer? In other words, is it not possible that his demands for efficiency would seem improbable of realization, if that were sought continually along the old lines, but by presenting a new criterion for the form of the illuminant, the illuminating engineer presents the clue to his own needs?

SUMMARY.

The general object of the presentation of these data and opinions, the latter largely quite personal ones, is to suggest the importance to all whose work deals with the production of light of a thorough acquaintance with the uses to which light is put and the methods of its use, that is—with illuminating engineering. The argument has been that only through the possession of such knowledge can the physicist or chemist who is studying light production hope to render his greatest service. It has been suggested how in several instances ignorance of the utilization needs might lead the investigator to overlook important contributions to the list of useful light sources.

A picture of the ideal light source has been presented chiefly noteworthy for its striking contrast with the ones in present use. In contrast with the brilliant point light sources now common the ideal one takes the form of a surface of low intrinsic brilliancy, perhaps in the form of a window shade, emitting light only in one hemisphere and unequally in different directions. It is of the appropriate color for the work in hand. Its efficiency will be expressed in figures comparable with those which exhibit the inefficiencies of our illuminants of today. These various demands, instead of being in conflict, may, it is pointed out, be mutually assisting.

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DISCUSSION.

Chairman Addicks: Unfortunately the illuminating engineer has had to compete with a standard of light established by nature, by which we have been not only governed, but perhaps prejudiced. At least, the engineer, having found that more or less monochromatic light can be more efficiently generated, has so argued and tried to persuade us that our preference to look pink rather than green was after all a matter of taste.

In recent years, however, the engineer is returning to more rational standards, and realizing that the sun is simply a ball of light hung high enough to be out of the way, now imitates this source, but being unable to hang it high enough turns it upside down against a screen to shield it.

Regarding efficiency, as I understand it the figures on the blackboard are stated in terms of energy applied at the lamp terminals, and the missing quantity is dissipated in wave lengths which can not be perceived by the eye. As the light is, therefore, a by-product, why should not we generate it as a by-product, but use the rest of the energy in some useful way, whether it be as heat or otherwise?

Jos. W. Richards: I wish to ask Dr. Ives what is the standard, that is, what is the actual energy equivalent of light to which he refers?

H. E. Ives: The mechanical equivalent of light is about 0.02 watt per candle-power.

Carl Hering: Dr. Ives in his extremely interesting and instructive paper has omitted mentioning one way of generating light which is at least theoretically possible. It is known that the electro-magnetic waves used in wireless telegraphy are physically the same as light waves, differing only in that the wave lengths of the former are immensely greater. If it were possible, by some physical means, to produce these electro-magnetic waves short enough, we could produce light directly.

Chairman Addicks: Does there seem to be any possibility of making a storage battery for light based on the luminescence of phosphorus?

H. E. Ives: Yes; a thought occurred to me which I had considered putting in the paper. According to a recent calculation one square meter of the surface of the streets of Paris receives from the sun in an hour, or some small time (I forget the exact figure), more light than the total artificial lighting system of the city gives in a year. It has been made sufficiently apparent, I think, that our methods of producing artificial light are not very far advanced. The possibility occurs to me, as it did to the Chairman, that a study of the processes of *storing* light might solve the problem very nicely for us. We are simply flooded with light which you can not use during the day time, and then at night we have got to burn up our natural resources in order to get back a relatively very small amount of light.

Chairman Addicks: The transformation of radiant energy has been tried, and to a certain extent it works; the trouble with the process is that it is of rather low efficiency, transforms down instead of up, and unfortunately most of the radiant energy is given off at frequencies below the visible spectrum. Ultra violet rays can be transformed into visible rays, but as yet we are not able to transform the low frequency heat rays into visible radiations. These transformers do not operate that way.

Carl Hering: Speaking about the transformation of the wave lengths of light, which is accomplished by a phosphorescent screen; such a screen is a true transformer of frequencies, or wave lengths. I understand from Dr. Ives that it is possible to thus transform them down to a lower frequency, but not up. It might be possible, therefore, to generate waves of a shorter wave length than light, and then transform these down to visible light by means of fluorescent screens, which I believe are the only transformers of the wave lengths of light that we now know of.

Chairman Addicks: As I understand it, we have certain chemical substances which practically store light on a small scale.

T. E. Moon: There are some very interesting phenomena connected with fluorescence that might be cited, and one is this: If you store say a unit of energy in a fluorescent screen, and let it shoot out into a dark room where there are no other light

sources of like value given off, there is a certain amount of energy at the top of the curve. However, if you subject it to any other radiation down in the ultra violet there will certainly be given off that amount of energy in a short space of time.

Jules Verne happened to be ahead of Dr. Ives about forty years with his luminescent ceiling, as you will remember in his "Twenty Thousand Leagues under the Sea." That is a very curious scheme and something which, from the illuminating engineer's standpoint, would be highly desirable for some installations. The monochromatic light source, while it gives much higher definiteness for sorting material, printing machinery and things like that, is not pleasant from the esthetic point of view.

In the case of the screen which Dr. Ives suggested to put in place of the window to draw down the light, it is difficult to see how he could obtain ideal distribution without enormous absorption. This follows from having a large source.

In the Lynn works I obtained an efficiency based on Dr. Ives' plan of 14 percent, using Cooper-Hewitt 4-inch (10 cm.) quartz tubes. The life was about 320 hours when getting this rate per watt. This is much higher than his 7 percent with the yellow flame arc. Moreover, it is a very steady light. We found, however, the disintegration of the cathode was carried at such an excessive rate that we could not get more than three hundred and twenty hours' life out of the tube. Where we have low intrinsic brilliancy, occasionally we find the watts per lumen are similar to his characteristics. When we have a high actinic source, shield that from the view of the person in the room, throw upon the ceiling or wall a shade, and reflect that into the room, we find it hard not only to get the extra efficiency of the actinic characteristic, but also loss in shadow is present, which will more than offset our present light sources.

Jos. W. Richards: It is my experience that using artificial light the ease with which the print is read is proportional to the way in which it contrasts with the paper; when you get too much light on the paper you see the print much less distinctly. My observation is that most people in using artificial light for reading use anywhere from two to three times as much light as gives the maximum contrast or clearness of visibility of the print.

I read with a low light, turned down to about one-half what

most people would use, and can then read for hours without fatigue. As soon as I turn the light up to what is considered the ordinary light for reading, my eyes quickly tire. My observation is that students, particularly, sin in that respect. They turn up the light until the amount of illumination on the page is so great that it dazzles and tires their eyes, and the clearness of the print is diminished thereby.

One of the chief objections I have against the electric light for reading is that you can not turn it down to the proper point. When reading, I increase the light until I get the maximum visibility of the print, which can not be done with the electric light.

CARL HERING: There is another factor bearing on this question of illumination which is often overlooked, although Dr. Richards just referred to it indirectly. The chief purpose of light is to enable us to see. Aside from its use for plant growth, photography and a few other purposes, the thing that we want light for most is to see by. Therefore the problem is one involving the human eye. If it were possible so to strain our iris that the pupil could expand still more than it does, we could see with less light, and would then need less artificial illumination; the action of the pupil is therefore a very important factor in determining the amount of illumination required at night. To a certain extent we can enlarge the pupil, hence it is really not necessary to have as much light at night to see by as we have in the daytime; it would be a waste of energy to illuminate interiors as much at night as they are illuminated in the daytime. Nature has provided us with this variable pupil; we can enlarge it at night, and can therefore see with less light. If you take a cat out of a dark cell and look at its eye quickly, the whole eye is pupil. If we could expand our pupils like that we would save much artificial light.

A paper presented at a meeting of the New York Section, November 10, 1914, in joint session with the American Gas Institute and the Illuminating Engineering Society, and called up for discussion at the Twenty-seventh General Meeting of the American Electrochemical Society, in Philadelphia, April 24, 1915, in Joint Session with the Illuminating Engineering Society.

CHEMISTRY IN THE DEVELOPMENT AND OPERATION OF FLAMING ARC CARBONS.

By William C. Moore.

In an arc struck between two carbon electrodes, very nearly all the light comes from the incandescent electrode tips. In a direct-current arc, the positive crater is larger, and possibly at a higher temperature than the negative crater, and it is this positive crater which is the source of most of the light. Since the crater is merely an incandescent solid, it affords a continuous spectrum; colorimetric experiments recently made by L. A. Jones, and reported by him at the Cleveland Meeting of the Illuminating Engineering Society, September, 1914,[1] show that this incandescent crater has about 67 percent of the daylight value of noonday sunlight. When volt-ampere readings are taken with such an arc, it is found that if the arc is lengthened, the voltage rises and the amperage falls, and eventually the arc goes out. If, as in the present instance, we use as one of our electrodes a carbon rod which has been hollowed out into a cup, and place in the cup some potassium chloride, and again strike the arc, we find that the volt-ampere characteristics are changed and that at the same amperage, a much longer arc can be drawn. Cassellmann in 1844[2] seems to have been the first to have noticed this fact. As we see, an arc fed with potassium chloride gives very little light; in fact, probably less than the pure carbon arc as the positive crater is not so bright. This arc has a distinctive color, and, of course, would show beside the carbon arc lines, the potassium lines in the spectroscope. Bunsen[3] in 1844, seems to have been the first to notice that different materials give different spectra in the arc.

[1] Trans. Illum. Eng. Soc., **9**, 687 (1914).
[2] Pogg. Ann., **63**, 576 (1844).
[3] Berzilius, Jahresbericht über die Fortschritte der Chemie und Mineral, **25**, 20 (1845).

If, instead of potassium chloride, we place a small amount of calcium fluoride in the hollow carbon cup, which, in this as in the previous case, is in the lower positive carbon, we find that the arc length for a given current and voltage is much shorter than for potassium chloride, and longer than for a pure carbon arc; moreover, the arc is intensely luminous, though rather unsteady and liable to go out. On placing a mixture of potassium chloride and calcium fluoride in the arc, we get the combined advantages of a long arc, with more intense luminosity than is afforded by either the pure carbon arc or the potassium chloride arc alone. These simple facts form the starting point in the development of the modern flaming arc. About 1899, Bremer, in Germany, brought out a flaming carbon, with calcium fluoride as the essential light-giving salt. The light afforded by such a carbon is a sensation yellow; the color is more aptly described however, as "minus blue," as the spectrum of such an arc is very deficient in the blue.

From 1899 to the present, the development of the flaming arc has been going on steadily and surely. It is interesting to note that the first record the National Carbon Company has of any work being done by them on the subject was when some ordinary cored carbons flamed and experiments were undertaken to prevent this phenomenon.

Although Bremer produced a carbon which could be burned vertically, for a number of years most of the commercial lamps were "inclined trim" lamps taking long, cored carbons, which burned under open-arc conditions. A few years ago, however, there was developed a lamp for burning flame carbons in a vertical position, and for these lamps solid carbons have been developed. An interesting point is that the idea of solid carbons antedated the development of the lamps. These lamps generally operate in such a way that a limited supply of air reaches the arc, that is, under "enclosed-arc" conditions. These various types of lamps are doubtless familiar to the illuminating engineers present.

Modern flame carbons may be classified in several ways. From the standpoint of the mechanical structure of the finished carbon, we have cored carbons and solid carbons. From the standpoint of the color of the light emitted by the carbons, we have a major

division in which are included yellow flame carbons and white flame carbons, and a minor division including red, green and blue flame carbons, red and green being but little used except for advertising purposes, and blue being used as a source of blue and ultra violet light for medicinal purposes.

In the major division, calcium fluoride is the chief constituent of yellow flamers, and rare earth compounds the chief constituents of white flamers.

A brief description of the method of manufacture of flame carbons may not be out of place. The first step, of course, is the careful weighing out of the requisite amount of the carbon base, and the proper flame materials for making a "mix." Most of these mixes are rather complex. After weighing, the ingredients are very thoroughly incorporated together and with an appropriate binder—generally tar, or pitch, or a mixture of these. The "mix" is then forced by means of a hydraulic press, into long rods, which after cooling are cut into the proper lengths. These green carbons are then carefully baked in gas-fired furnaces and the temperature gradually raised according to a definite schedule, the final temperature attained being determined by a number of factors, such as the liability of some of the constituents to volatilize, or to react with each other and the carbon.

After cooling the furnace, the carbons are unpacked, sorted, cleaned and gauged, the latter process consisting in determining the diameter, as but small variations in diameter are permissible; the carbons must also be quite straight. Some solid carbons are electroplated with copper on the holder end to make a better contact between the lamp holder and the carbon. After plating they are dried and made ready for shipment. It is, of course, necessary to keep all flame carbons dry, as water may cause reactions between some of the flame materials, or may set up a carbon-copper cell with some of the soluble or partially soluble salts as electrolytes and thereby destroy the copper coating. Water has another detrimental effect as shown by W. R. Mott,[4] namely to react with the carbon at high temperatures, forming carbon monoxide and hydrogen; the latter may not only accumulate in the lamp housing and cause the lamp to explode when

[4] Mott, Electrical World, Dec. 13, 1913, p. 1220.

started again, but rapidly conducts heat away from the burning arc and lowers its efficiency.

The manufacture of cored carbons is quite similar to that of solid, except that the carbon base is different, and in forcing the die contains a pin which makes the carbons hollow. After baking, sorting and gauging this core hole is filled with a mixture of a carbon base and the flame materials with an appropriate binder, and the carbons are then dried. As cored carbons are usually very long and of small diameter, a zinc wire is inserted into a small hole parallel to the core hole. This wire increases the conductivity of the carbon. In order to make a good contact with the carbon and the holder, the carbons are "silver tipped"—that is, first copper plated, then dipped into solder, which solders the zinc protruding from the holder end, to the carbon. Such a connection is a permanent one, and is far superior to the scheme of simply bending the zinc over at the end of the carbon, as the zinc becomes brittle when the core is dried and is liable to break off.

We now come to the question of desirable operating characteristics for a flame arc carbon. First of all, such a carbon should be reliable. It has been pointed out by Steinmetz[5] that after high efficiency is attained, we can afford to sacrifice some of the efficiency for reliability, and other desirable factors. As will be shown below, the flame arc is already of high efficiency, hence we place reliability as our first desirable characteristic.

We may consider reliability under the four heads:

1. Constancy of distribution.
2. Constancy of light flux.
3. Constancy of color.
4. Ability to start with cold points after the carbons have been in use.

The length of the arc has a great deal to do with the amount and distribution of light. As the arc lengthens, the voltage increases; it is stated by Hechler[6] that there is a maximum definite voltage for maximum efficiency; that is, some definite arc length gives the most light.

[5] Gen. Electric Review, **17**, 180 (1914).
[6] Abstract in "Electrician" (London), **69**, 658 (1912).

The part that chemistry has had in increasing the reliability may be briefly indicated. It is readily seen that a flame arc which burns brightly part of the time and dimly part of the time can hardy be said to have 100 percent reliability if all the other factors are high. It may happen that all the flame material is evaporated from a given spot on the surface of the carbon, thereby causing a pure carbon arc for a short time. Such changes, however, are now rare, as a great deal of constructive chemical work has practically obviated this feature.

Another factor affecting the reliability of operation of flame arc lamps is the formation of slag on the points or on the lamp mechanism, and it is readily seen that the proper proportion of the flame constituents and the right kind of addition agents for preventing such slags are of great importance. Here again we find that extended chemical research has resulted in the development of carbons in which this source of trouble has been largely overcome.

It has been mentioned that the flame-arc is of high efficiency. The following figures are from some regular routine tests made in the laboratory.

Lamp	Current	Kind of Carbon	M. S. C. P.	Arc Watts	Watts per Candle
Excello	A. C.	Cored—yellow	1,220	363	.29—
Excello	A. C.	Cored—white	843	369	.43—
Excello	D. C.	Cored—yellow	1,462	445	.30
Excello	D. C.	Cored—white	875	450	.51
G. E., Type W	A. C.	Solid —yellow	700	397	.56
G. E., Type W	A. C.	Solid —white	808	394	.49
G. E., Lynn	D. C.	Solid —yellow	1,181	409	.35—
G. E., Lynn	D. C.	Solid —white	939	421	.45

The candle powers as given are at the arc.

The slightly lower efficiencies with the solid carbons are due to the fact that they are used in enclosed lamps, to which the air has only limited access and so in these lamps there is less oxidation of the carbon and the flame material.

Some work by Henry P. Gage[7] at Cornell University on the efficiency of the arc stream proper may be cited here. This investigator found that, with cored yellow-flame carbons the energy radiated as light from the arc stream was 39 percent of the total energy radiated by it; with the arc stream from covered white

[7] Phys. Rev., 33, 111 (1911).

flame carbons, 27.5 percent of the energy radiated by the arc stream was light energy. The entire yellow arc showed 6 candles per watt radiated, while the entire white arc showed 3 candles per watt actually radiated.

These values are for the spectral region between 3,800 and 6,800 Angström units, and for alternating current, at 13.5 amperes.

The following data may be presented as to the life of flame carbons:

	Life in Hours	
	A. C.	D. C.
Cored—yellow	12.0	12.50
Cored—white	11.08	11.25
Solid —yellow	115.08	125.0
Solid —white	120.0	96.42

The values for cored carbons are based on 400 mm. "trims."

These figures show why the enclosed flame arc lamp is more popular than the old "inclined trim" lamp, using cored carbons.

Having indicated at a number of points the important part chemistry has played in the development of the modern flame carbon, let us now take up in greater detail some of the chemical aspects of our topic.

In the first place, the selection of the proper materials for the manufacture of flame carbons is to a very large degree dependent on the chemical properties of these materials. When we consider the carbon base, we find that the chemical behavior, as well as the physical behavior of the various so-called forms of carbon differs with the type of carbon employed. To use an extreme case as an illustration, we know that the chemical properties of graphite differ greatly from those of lampblack. There are likewise similar differences between charcoal and lampblack; petroleum coke and retort coke. This in part accounts for a different carbon base being used for solid and for cored carbons.

To a greater degree than the proper selection of the right carbon base, the selection of the right sort of flame material and the right sort of addition agents with this flame material has been a chemical problem. This is illustrated by the fact that today we know no better material than calcium fluoride for the main constituent of yellow flame carbons. I do not think I will exaggerate the matter in the least when I say that compounds of every compound-forming element have been proposed as proper sub-

stances to incorporate into flame carbons—some of them in all sorts of possible and impossible combinations.

Having selected the right materials, the right amount of each is our next chemical problem. That the candle power depends upon the amount of flame material is well known; more exact information on this subject, however, may be had from the following table which is from some work done in our Research Laboratory by Mr. Wm. R. Mott, using cored carbons in an Excello direct-current lamp:

Parts of calcium fluoride by weight....	3	2	1	0
Parts of other salt by weight.....	0	1	2	3
Mean spherical candle power (delivered).	927	1,058	765	574

As is seen, there is a maximum percent of each of the constituents which will give the most light. This is true with nearly every substance which may be added to the calcium fluoride, and when we consider that flamers contain three or more substances in addition to the main constituent, it is readily seen that the nice adjustment of all these substances to each other presents some very interesting problems. It also explains why so much of our knowledge has been obtained in an empirical way. It is, of course, understood that the maxima for different addition agents do not coincide.

The chemical control of the impurities present in the raw materials is of great importance. Silica, ferric oxide and alumina, as is well known, are common impurities in calcium fluoride, and it so happens that too much of these impurities will make a poor burning carbon. Silica is especially undesirable as calcium silicate is very non-volatile and so is a frequent cause of slag formation. The analytical difficulties in determinations of fluorine, silica and rare earths in presence of each other and of carbon are very great.

The unbaked carbon is a poor conductor of electricity. It is also rather friable. In the baking, the binder is coked and the carbon is rendered homogeneous and conducting. This coking of the binder is the chief chemical change occurring in the manufacture of the carbon.

We now have to consider what chemical changes may occur during the burning of a flame carbon, and how these may affect the light emitted from the flaming arc. There are three possible sources of light in the flaming arc: electro-luminescence, thermo-

luminescence, and chemi-luminescence. We do not know to what extent these three factors affect the light radiation in any one case. We do know, however, that in general, there are two types of flaming arcs, (1) those in which the outer sheath seems to be intensely luminous, (2) those in which the core of the arc seems to be more luminous than the sheath. With very few exceptions arcs of the latter type give light of the shorter wave lengths. An arc into which calcium fluoride is introduced is a representative of the first type; an arc into which chromic oxide is introduced is of the latter type.

King has recently reported[8] that in a tube furnace almost all of the spectral lines seen in the arc spectrum of titanium appear, so that it would appear that in some cases a large proportion of the light from an arc is due to thermo-luminescence, though all possibility of chemical change was not precluded by these experiments.

Oldenberg[9] has made a spectro-heliographic study of various arcs, with some interesting results: For instance, he concludes that in the sodium arc, lines belonging to the principal series such as the "D lines" are due to chemical reactions between the vapor and the air. Band spectra seem to be of two types: those of the first type are due to collisions of atoms in the high-temperature core of the arc. The cyanogen bands always seen in a carbon arc he ascribes to collisions between carbon and nitrogen atoms. Bands of the second type are found in the sheath of the arc; they are due to undecomposed molecules; the bands of the calcium fluoride spectrum are of this type. When we consider that the flaming arc is a miniature electric furnace; that Fremy[10] showed years ago that oxygen converts calcium fluoride into calcium oxide; that calcium oxide and carbon react to give calcium carbide and carbon monoxide, and that the other constituents of a flame carbon may react with calcium fluoride, with the carbon, with each other and the atmospheric gases, we see that it is possible for chemical changes to play an important part in the production of the light of the calcium fluoride arc. Each of the possible substances may play its part in this light emission.

[8] Astro-physical Journal, **39**, 139 (1914).
[9] Zeitschrift für Wiss. Photog., Photophysik und Photochem., **13**, 133 (1913).
[10] Ann. Chim. Phys., (3) **47**, 17 (1856).

In conclusion, I think we may safely say that the past progress made in the flaming arc art has been due to the co-operation of the chemist, the physicist, and the electrical engineer; the future progress will likewise be dependent upon their combined efforts.

It might not be out of place to point out that the behavior of any one substance in the arc is determined by the conditions surrounding that substance—it behaves according to definite chemical and physical laws; and that our knowledge of these laws for high temperatures is exceedingly meager. On the other hand, once these laws are learned, it will probably be easier to build lamps to suit the carbons rather than to make a carbon to fit any and every lamp. In the extension of our knowledge of these laws, chemistry and especially physical chemistry will play an important part. If I have succeeded in showing you that without the aid of chemistry the development of the flame carbon would have been well nigh impossible, I shall feel that my labors have not been in vain.

I wish to thank the Illuminating Laboratory for the data on candle power and life.

Research Laboratory,
National Carbon Company,
Cleveland, Ohio.

DISCUSSION.

W. R. Mott: The flame arc is a very complex problem and there is no known limit to its efficiency or future development. The incandescent lamp seems to have reached its limit in the use of tungsten at a few hundred degrees below its melting point. Referring to inclined trim carbons I have made by suitable additions carbons with 70 percent greater candle power than possible by calcium fluoride alone. As Dr. Moore points out there are three sources of light in the flame arc—heat luminescence of carbon and flame materials, chemical luminescence and electro-luminescence. In the mercury arc the electro-luminescence is all important since chemical luminescence is precluded because of the known atomic condition of the mercury vapor and absence

of other reactive elements. Atomic disintegration, and electronic phenomena are electrical and can be called chemical but not in the ordinary sense of combinations between atoms. Heat luminescence of mercury is very small. Paternö and Mazzuchelli (Atti. Accord. Lincei **17**, II, 428-32) have tested the emission spectra at high temperatures of mercury, selenium, antimony, etc. Selenium gave a white light. Antimony gave a band spectrum, but mercury vapor remained dark. Child's experiments are very convincing as to electro-luminescence of Hg. In the titanium arc, Steinmetz lays great stress on electro-projection from the negative electrode and hence maximum electro-luminescence. That chemical reaction is present is very evident because Ruff and others (See Z. anorg. Chem., **82**, 373 (1913) have shown on heating TiO_2 the formation of the lower oxides of titanium. Also titanium nitride is one of the products of the titanium arc. However, most of the light probably comes from the electro-luminescence.

In the calcium fluoride arc, the material is conveyed to the arc largely by heat vaporization according to Steinmetz. The yellow shell of a yellow flame arc can be made to appear also in the midst of the blue core by using a solid hollow yellow flame carbon and high current so that the crater covers the end. Rossi (Proc. Roy. Soc. (London) A, **82**, page 518) has treated the influence of pressure upon the band spectrum of calcium fluoride and other alkaline earth fluorides. This work followed up that of Dufour (C. R. **146**, p. 118) on the Zeeman effect in calcium fluoride arc. Rossi says "The banded spectra of these fluorides are almost entirely due to light emitted by the outside layers or flames of the arc. Under pressure, the arc shortens very much, at 50 atmospheres, it is only a few millimeters long." The bands which show the Zeeman effect are also displaced, by pressure which with calcium fluoride is proportional to magnetic separation. Koenigsberger and Küfferer (Physik Z., **11**, p. 568) have developed a theory about the relation of band spectrum and chemical dissociation. This works out very well for iodine dissociation. In my experiments on calcium fluoride in different atmospheres, spectrum examination shows marked differences due to chemical reactions. I can not enter into details owing to the

commercial nature of the researches. In the arc, we can expect a great variety of chemical reactions. For example calcium subfluoride is very stable at high temperatures as shown by Ruff. The chemical luminescence is undoubtedly the most important factor in the yellow flame arc.

G. S. Barrows: We are all very much interested, of course, in the question of light production, and in the efficiency of light production. Dr. Ives pointed out this morning that we are down below where we should be. If it may be possible with arc lamps, with the proper flame carbon, to get a desirable color of the light by the change of ingredients of the carbons, or proper mixtures in the ingredients, it seems as though it will be a tremendous step in advance.

We are engaged now on problems concerning the proper quality of light. It is astonishing how many cases come up. For instance, there is one right here in the University of Pennsylvania. In the new Architectural Building, which is the old Dental Hall, north windows are the desirable windows for the life-study room, where colored wash drawings from nature are made. For this purpose it is necessary to have the colors in their true light. As these north windows face the Engineering building, which has a red brick wall, they have to keep their window down to prevent the red reflection from the engineering building from getting into the drawing room.

This is only one of thousands of similar problems which are coming up all over the country today, and we feel that, aside from the question of the efficiency of light production, the question of the quality of light production is one which should be given very careful consideration and it seems to us that it is a chemical as well as a physical problem, which may be very well considered by the American Electrochemical Society.

W. S. Franklin: All of the terms in which *luminescence* or *phosphorescence* are used are terms that are intended to designate that type of radiation which departs from normal heat radiation, and the term thermal luminescence was originally applied to the pale blue light which is given off, for example, by fluorspar when it is heated. Whereas I think you intended, in using the word thermo-luminescence, to designate that part of

the radiation of the arc which is due merely to the high temperature.

G. S. Barrows: Exactly.

W. S. Franklin: I think you should call that simply heat radiation, or normal heat radiation. Chemi-luminescence does no doubt take place in the arc, and there is certainly something in the arc which may be called electro-luminescence, because the radiation from the arc departs from normal radiation corresponding to its temperature. That is, the radiation from the arc departs from the normal radiation corresponding to its temperature, on account of the chemical and electric actions which take place. It is proper to use the words "chemi-luminescence" and "electro-luminescence," but I do not think that your use of the word "thermo-luminescence" is in accord with common usage.

Carl Hering: In view of the fact that this paper recites the history of the flaming arc, I think it should not be left unsaid that Dr. Edward Weston, one of our members, was really the first one to invent the flaming arc. There was a patent issued to Weston in the seventies, hence nearly forty years ago, for introducing various chemicals into the carbon rods of the arc lamp, in order to get more light. The credit is usually given to Bremer, a German, who introduced such lamps in 1899; but as a matter of fact this improvement was invented in America about twenty-four years before Bremer brought it out. I think Bremer is given the credit for it in Germany.

In connection with what Mr. Barrows said, it seems to me it would help matters very much if that one wall of the engineering building were painted white.

W. A. Darrah (*Communicated*): In connection with the very excellent paper by Mr. Moore, there are a number of points in which the lamp designer and the carbon manufacturer should co-operate in order to secure the best results to the final user of the lighting apparatus. As the paper touches upon a few of these points it seems pertinent to bring out the lamp manufacturers point of view.

In connection with Mr. Moore's clear discussion of the differences in the performances of flame carbons and solid plane

carbon arc lamps, it may be of interest to note a few photographs of various types of arcs.

Fig. 1 shows the arc between solid plane carbons in a 6.6 ampere alternating current enclosed carbon-arc lamp. This figure emphasizes the point brought out in the paper that the light comes largely from the incandescent tips of the carbon electrodes. This photograph is somewhat misleading in that the arc appears rather more luminous than it actually is, because of the excess of ultra-violet light which very readily affects the photographic plate.

Fig. 2 is a photograph of an enclosed solid-flame carbon arc in a 6.5 ampere direct-current lamp. The absence of luminosity

Fig. 1.

of the electrodes is quite noticeable. One notable and interesting characteristic is that the shape and appearance of the arc is more largely determined by the effect of air currents and adjacent magnetic fields, than by the polarity of the electrodes or direction of flow of current. It is a peculiar fact that it is practically impossible to tell from an inspection of this arc which electrode is positive and which negative. The cup shape surface which shows above the arc is a portion of the soap-stone economizer and will be discussed later.

Fig. 3 is a photograph of a solid flame carbon arc in a 10-ampere alternating current lamp. The shorter length and more compact structure of this arc are due partly to the higher current

and partly to the fact that it is supplied from an alternating current source instead of a direct current source. The intensity of the direct current and alternating current flame carbon arc is approximately the same, any difference in the figures being due to differences in the photographic conditions.

Fig. 2.

In connection with the requirements of a good flame carbon, it has been the writer's experience that the following features are of considerable importance to the user of a lamp.

1. A high luminous efficiency.
2. Minimum operating difficulties.
3. A long life.
4. Steadiness of operation.

The efficiency of the flame carbon is almost entirely in the hands of the carbon manufacturer, and the lamp manufacturer

can have but little influence on this feature; all of the other factors can be obtained by co-operation between lamp manufacturers and carbon manufacturer.

Our experience with flame carbons indicates that the troubles which have been occasionally charged against them may be appreciably reduced or even eliminated by proper attention on the part of the operating man; thus, if the lamp user will take care that the globes seat tightly, that there is no way for air or moisture to enter the globe, and will clean the lamps properly at

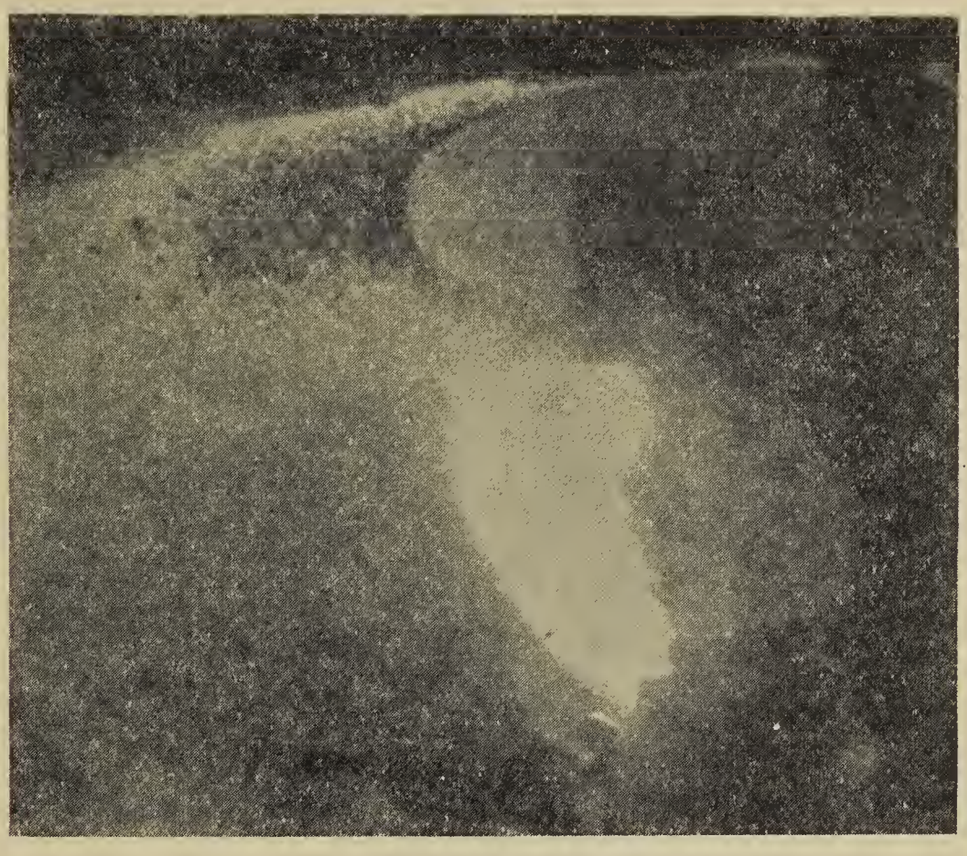

FIG. 3.

the time they are trimmed, their performance will be much improved. The few cases in which operating difficulties have been reported appear to be traceable to causes of this nature. Such factors as a large fluctuation of terminal voltage, variations in frequency, or reversal of the current in the direct current circuit must be considered before the carbon or the arc lamp is blamed for the troubles that are encountered.

The life of a solid flame carbon in commercial arc lamps varies from 100 to 130 hours, depending upon operating conditions and the attention given the lamp.

In this connection it might be of interest to consider Fig. 4, which shows in a schematic way the general arrangemment of the arc, economizer and globe of a flame carbon arc lamp. Contrary to the usually accepted opinion the design of the lamp, especially such points as the position of the arc with relation to the globe and condensing chamber, as well as the shape and position of the economizer, may have a very considerable effect on

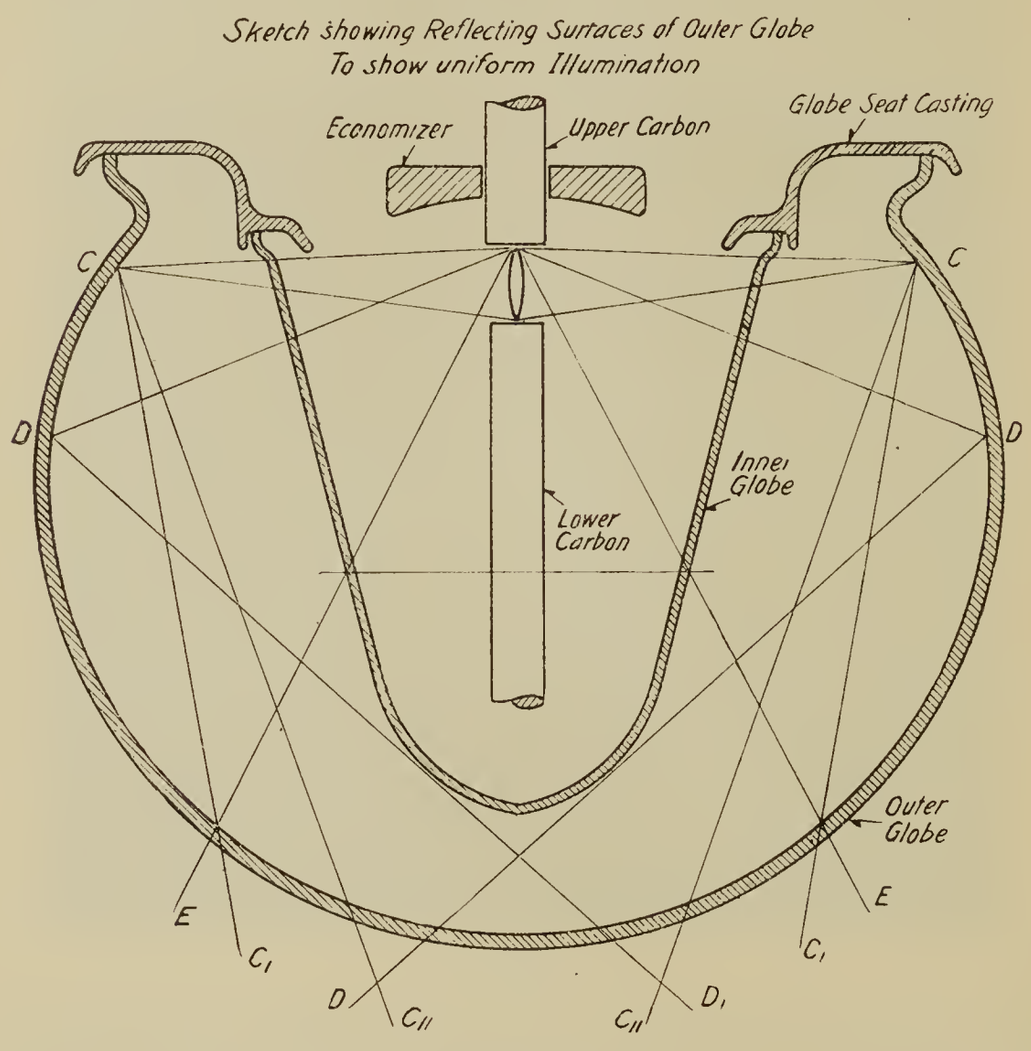

Fig. 4.

the life of the carbons, as well as on the relative rates of consumption of the upper and lower carbon. Thus in a certain large negotiation for flame carbon arc lamps in which the writer was interested it was found that the life of a given type of carbon in a competitive lamp was materially less than the life of the same carbons in the lamp in which the writer was interested. Voltage, current and operating conditions were obviously identical and after some investigation it developed that the shape of the econo-

mizer which was placed above the arc and the distance between the arc and the economizer largely accounted for the abnormal condition of the carbon life. In this instance the differences amounted to over 30 percent in tests which we made on several hundred lamps.

It will, of course, be obvious that any construction which tends to reduce the air currents, and prevent the passage of gases over the heated electrodes will increase the carbon life.

Fig. 5 shows a view of type of lamp which has a life from 110 to 130 hours under normal conditions, while Fig. 6 gives a detail of the construction of the economizer of this lamp and its position with relation to the arc.

In connection with the discussion of carbon life it might be of interest to recall that the average life of a carbon in a multiple lamp either alternating current or direct current is less than the average life of the same carbon in a series lamp, for the reason that the somewhat greater stability of the series lamp reduces the amount of "pumping," i. e., restriking of the arc, and therefore tends to reduce the amount of outside air which enters the lamp. It is a peculiar fact that the striking of an arc within a closed chamber instantaneously materially increases the pressure within the chamber, and the extinction of the arc instantaneously reduces the pressure, showing that this effect is independent of temperature. The marked variations of pressure within the arc chamber naturally tend to expel the air within the chamber and allow fresh air to enter when the arc is momentarily extinguished.

In actual practice there appears to be a very slight difference between the life of carbons when operated on direct current circuits or alternating current circuits, providing the total wattage is approximately the same. There is, however, a tendency for yellow carbons to have a somewhat shorter life than white carbons, although this, of course, varies with the different types of carbons.

In Fig. 7 the dash-dot line shows the distribution of light from the flame carbon arc lamp under commercial operating conditions. This curve was secured from a lamp equipped with clear globes and without reflector. The use of Alba or other diffusing globes has an effect of changing the curve to the shape shown

by the broken line, in Fig. 7; in other words, the globe becomes a secondary light source, thereby directing the light in directions which were previously not so well illuminated.

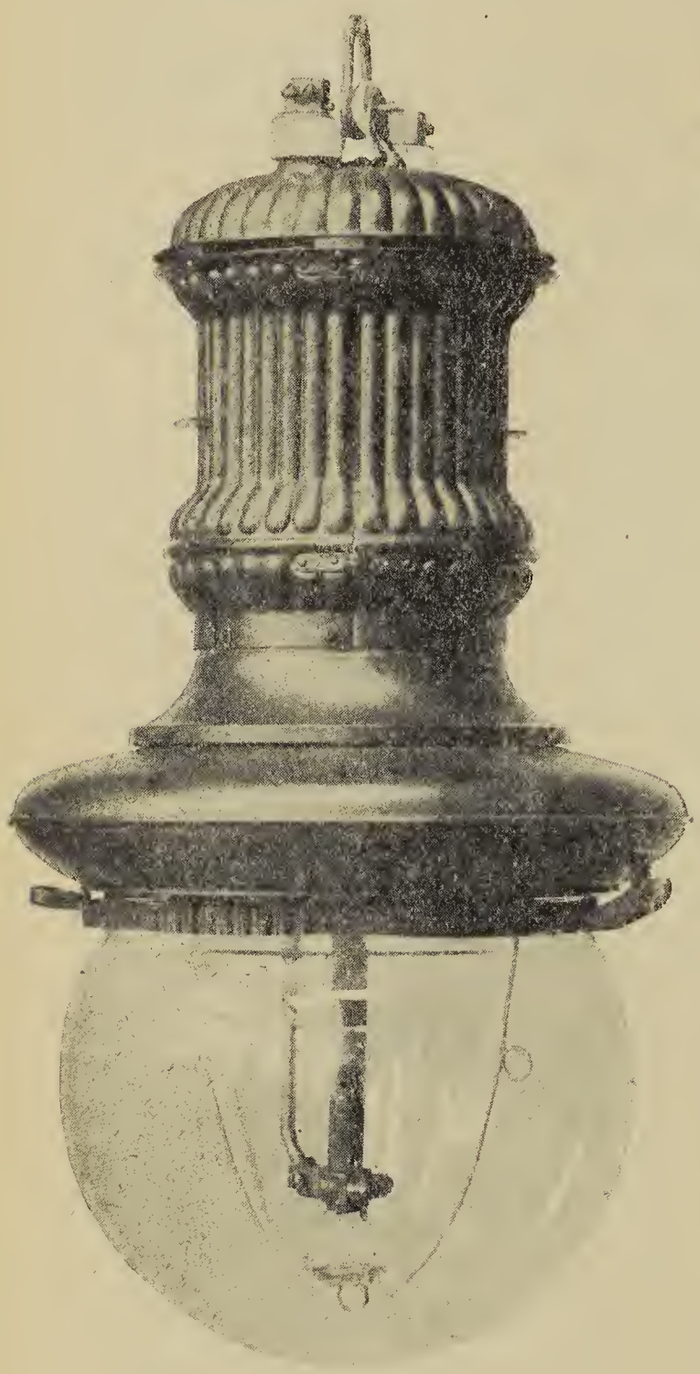

Fig. 5.

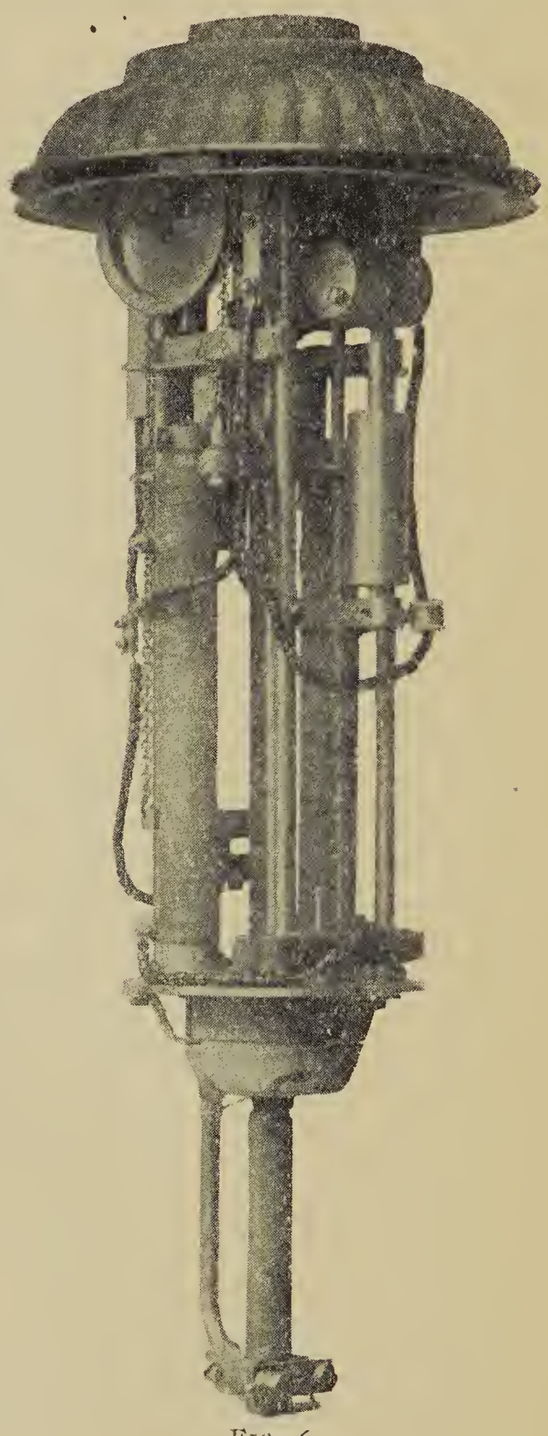

Fig. 6.

The continuous line shows the effect of applying a porcelain enameled reflector to the same type of lamp as that shown by the other two lines. A consideration of these curves will indicate that the arrangement of globes and reflectors has more effect upon the light distribution than the characteristics of the car-

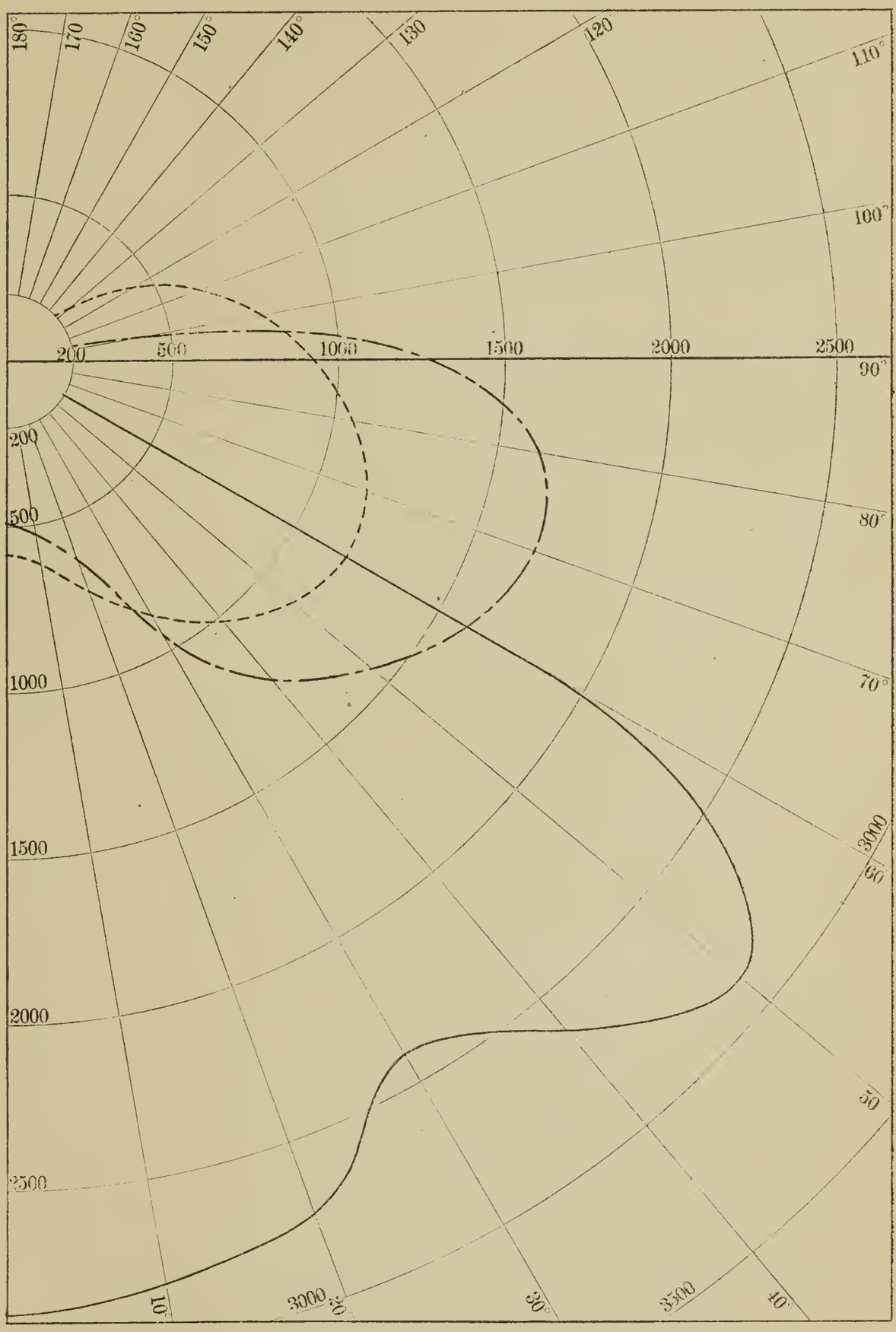

FIG. 7.

Dot-dash line: Inner globe clear, outer globe clear.
Broken line: Inner globe clear, outer globe alba.
Full line: Inner globe clear, outer globe absent, and enameled steel reflector used.
All other conditions of lamp practically alike.

bons. In passing it is of interest to note the large amount of absorption which results from the use of diffusing globes. It is unfortunate that the carbon manufacturer should be forced to expend considerable time and money in increasing the efficiency of his output a few percent and then have the whole gain absorbed by the use of inefficient diffusing glassware. It is the writer's feeling that the production of glass having a low absorption and a high degree of diffusion affords a large field for chemical research.

In conclusion the writer wishes to suggest that the greatest progress will be made in the shortest time by the closest possible co-operation between the carbon manufacturer and the lamp manufacturer. Whether further extension of our knowledge of the laws governing light production will result in the development of a lamp to suit each type of flame carbon, or the development of a carbon to suit each type of lamp, is a detail. The ultimate object of all progress is to benefit the final users of the apparatus.

C. G. Schluederberg: There have been many cases of trouble with arc lamps, due to reversal of current where, unknown to the man in charge, the lamp had been connected up wrong.

W. Lash Miller: On page 437 we are told that rare earth compounds are the chief constituents of white flamers. I suggest that when this paper is printed the actual rare earth compounds and the quantities used be given in the appendix, in the interests of the National Carbon Company, because no one can think that a serious competitor of the carbon company would not buy these carbons and analyze them. It is quite impossible to conceal that information from any serious competitor, but any member of this Society who might be attracted to this subject by this paper, and wished to make any experiments, would want to begin where the National Carbon Company left off, he would not wish first to spend a week in learning how to make an analysis, and another week in making the analysis. This is all right for a competitor, but not for us, and by withholding this information the National Carbon Company does itself out of the chance that some member of the Society would be interested in the subject and would make some further experiments which might perhaps, possibly

only to a slight extent, improve the efficiency of these arcs, and in that case I think such an investigator would be sure to go to the National Carbon Company with his discovery, because he would know about their carbons, he would know he had a slightly better one, and he would be as apt to get $10 out of them as out of anybody else. It seems to me that in concealing information that can certainly be and will be obtained by their competitors, the National Carbon Company is acting contrary to the best interests of all concerned.

C. G. FINK: I would ask Mr. Mott if any extended investigation has been made on the gaseous products formed by the flamers. I imagine it does not interest the National Carbon Company very much what these gaseous constitutents are, except in so far as they attack the glass of the globe.

The point is, that the study of these gaseous products opens up to a very nice field for the University. The material is all in convenient form, the National Carbon Company would be glad to supply the electrodes, and the University would find the study of the composition and the properties of these volatile compounds highly interesting.

I am also curious to know whether any of these cored carbons, or these compound carbons have ever been tried out in electrolytic work or in electric furnace work. It seems to me here is another field which might be investigated. The application of the lighting carbons to other fields might eventually be more important than the present application in illumination.

T. E. MOON: I do not quite see how the lighting efficiency of the plain carbon would very much affect the efficiency of the electric furnace. That is purely a matter of heat characteristic.

C. G. FINK: The conductivity of the gaseous products is increased.

T. E. MOON: You do not get any higher temperature characteristic.

There is just one point I want to make a remark upon, referred to by the gentleman from Pittsburgh. He mentioned the Alba glassware. The Macbeth-Evans Company have a new glass on the market which the Electrical Testing Laboratories tell us absorb 6.8 percent. I am sure you will agree with that, because

the Electrical Testing Laboratories are absolutely authoritative, and I think that further progress will be made with this Alba glassware, which has beautiful diffusing characteristics. It is just as diffusive as other types of glass, and absorbs only seven percent of the light. It is called Maxon, or some such name as that.

Jos. W. Richards: When a closer study of the chemistry and physics of these flaming arcs is made, we will find a great lack of necessary physical data, such as the latent heat of vaporization of the different salts. Even the latent heat of vaporization of carbon is only guessed at so far, and yet it plays a large part in the condition or nature of the arc. Here, again, the Bureau of Standards or our Universities should determine some of these absolutely necessary fundamental physical constants.

Wm. R. Mott: As to Dr. Franklin's question on thermoluminescence, the term is here used (contrary to definition in books on physics) in the sense of light due to temperature radiation.

I am very much pleased to see how much interest the Westinghouse Electric and Manufacturing Company, as well as the General Electric Company representatives, have taken in discussing this paper, and I am sure that we all appreciate the necessity of co-operation between the glassware manufacturers, the lamp manufacturers and the carbon manufacturers.

The high efficiency of 94 percent light transmission through glass, reported by Mr. Moon, recalls laboratory tests where half the light was lost with clear inner and dense outer, due to glassware alone. The problem is to secure good transmission and to eliminate glare.

Dr. Fink's remarks are very interesting and very important as they open up a great variety of uses. In fact, I imagine a dozen papers could be written on the potential possibilities contained in the flame arc. There are thousands of chemicals we have experimented with and thousands we have not, and taking combinations of say ten or twenty of these at a time you get near infinity very quickly.

Referring to the gaseous reactions, we have been doing some work especially with the spectroscope. Calcium fluoride can

react reversibly with oxygen to give calcium oxide and fluorine. (No fluorine remains at ordinary temperatures.) The fluorine can unite with the carbon and silicon to form tetrafluorides and subfluorides. The calcium oxide can react with carbon and nitrogen to form calcium carbide and cyanamide. The carbon reacts to form cyanogen (which is shown by its spectrum). Many complex reactions take place in the flame arc, but due to their reversal they are difficult to follow.

Dr. Fink has suggested certain uses for the flame arc for which there is a big field. The flaming arc has a characteristic which is entirely different from the carbon arc. The flaming arc has favorable characteristics for easy electrical control. It will start at half the initial voltage of the carbon arc, and for like increase in voltage increases in length over twice as much as the carbon arc. This is favorable to the use of two flame arcs in series on 110 volts, and in electric welding to the use of low arc voltages. The possibilities of putting chemicals in carbons for electric furnaces have only been touched on.

I want also to call your attention to the use of the light of the flame carbons for chemical processes. With a 25-ampere white flame, you can get 5,000 mean spherical candle-power at 55 arc volts. The photographic power is four or five times as great as nitrogen incandescent lamps, or the mercury arc, or possibly any other form of illumination for equal total power consumption.

W. C. Moore (*Communicated*): Mr. Darrah brings out a number of important points in his discussion. We are glad to see that the experience of the lamp maker is the same as that of the carbon maker, with respect to operating troubles, *i. e.*, that many of the troubles ascribed to the carbons or the lamps are really due to lack of proper care by the user of the lamp.

His suggestion that the production of a more suitable glass for arc lamps affords a large field for research, is exactly to the point. That the gases sometimes attack the globe should be considered in such a development.

It is perfectly true, as Dr. Miller suggests, that our competitors have probably bought and analyzed our carbons, but that does not tell the whole story. It must be remembered that in solid impregnated carbons the light-giving salts are added before the

carbon is baked. The exact proportions in which these salts are to be added, and the kinds of salts, have, in general, been learned only after much extended and expensive investigation.

An analysis of the commercial carbon will not necessarily give these proportions, and I fear that any investigator who based his hopes of improving our carbons on analytical data alone would be doomed to disappointment. To solve completely our flamer problems will require the resources not only of analytical, but physical, organic, and inorganic chemistry as well. In this connection it might be well to point out that at present a portion of the writer's staff is engaged solely on the fundamental problems involved in the flaming arc, and that the problems are sufficiently numerous to keep several people busy for a number of years to come. We feel that we have barely scratched the surface in our flaming arc work. Moreover, it is pointed out, on p. 441 of the paper, that the analytical difficulties in the control of the raw materials are very great, and commercial calcium fluoride was given as an example. These difficulties are enormously increased in the baked or in a partly used carbon, due to reactions having occurred between the constituents. To interpret the data of analyses of commercial carbons requires considerable experience with this sort of work, so the information we would have to give Prof. Miller's hypothetical investigator is exactly the information we can't disseminate, because it would be exceedingly useful to our competitors. I can say, however, that the National Carbon Company will be glad to co-operate in any reasonable way with any one who wishes to experiment, not only with our flame carbons, but also with any of our other products.

As Mr. Mott pointed out, Dr. Fink's suggestions open up a great variety of uses for flame carbons.

Prof. Franklin's correction of my use of the term "Thermo-Luminescence" is acceptable, and I wish to thank him for it.

A paper presented at the Twenty-seventh General Meeting of the American Electrochemical Society, in Philadelphia, April 24, 1915, at a Joint Session with the Illuminating Engineering Society.

LIGHTING OF ELECTROLYTIC TANK ROOMS.

By R. E. Harrington.

Industrial lighting is a problem which, at the present time, is receiving considerable attention. Not alone does this apply to artificial lighting, but also to natural lighting, as is evidenced by the fact that the buildings are now being constructed with large window areas. Likewise, for artificial lighting it is significant to note that the standard is rising rapidly, so that what was good practice five years ago is now considered inadequate for efficient operation of plants.

The object of this paper is to bring to your attention reasons for, and results secured by, correct lighting, as well as lighting equipment available and means of arriving at the desired end.

Relations Between Light and Production.

In electrolytic tank rooms the nature of the process frequently requires considerable overtime work, and in some cases continuous operation. By providing correct illumination, the hours of efficient working are increased. That is, it is possible to work during the hours of darkness or diminishing daylight almost as effectively as during the rest of the day. Another advantage is that during the periods of rush it is possible to operate the plant overtime at full speed.

The question of the quality of the finished product must also be considered. Everyone realizes that there is always a certain percentage of work which is not first class, or has some imperfections. This product must be discarded or else sold as seconds at a reduced price. Experience has shown that a properly lighted plant has a marked effect on the reduction of this class of product.

Relations Between Light and Safety.

This is the age of the great "safety first" movement. Any person, be he employer or employee, who has given this problem thought readily admits that light is a great factor in the reduction of accidents. In the particular industry under consideration, some of the accidents are due to improper lighting, resulting in the inability of workmen to see clearly. The following are some of the most common accidents resulting from the above:

(1) Falls from narrow passageways around the tanks into the acid.

(2) Injuries from moving cranes.

(3) Falls in stairways and landings.

(4) Burns from bad electrical connections.

(5) Injuries from dangerous machinery and belting.

In this connection it is well to note that such accidents are frequently attributed to other than the principal cause—namely, poor lighting.

The curve in Fig. 1 shows the results of an extended investigation of the relation of daylight to accidents. This was taken from a paper presented by R. E. Simpson, and appears in the 1914 Transactions of the Illuminating Engineering Society, Vol. IX, No. 5, page 460: Each point on the curve represents the combined number of accidents for a period of three years for each of the individual months. This investigation, carried on by John Calder, covered about 80,000 industrial plants. From this curve it will be seen that during the months of shorter daylight the accidents rapidly increased.

The curve *X B C D Y,* in Fig. 2, shows the number of hours of darkness in each calendar day of twenty-four hours, the word darkness meaning the period between sunset of one day and sunrise of the next. Assuming that the length of night will have no influence, as long as the period from sunrise to sunset exceeds twelve hours, the horizontal lines *AB* and *DE* have been drawn. Comparing the curve *A B C D E* with that in Fig. 1, we at once see the similarity. This shows that proper lighting has a very marked effect on the number of accidents. Accidents

are not only expensive, due to claims, etc., but they have a demoralizing effect on the workmen, often resulting in decreased production. If the number of accidents can be decreased by good lighting, this should be done from a business, if not from a humanitarian, standpoint.

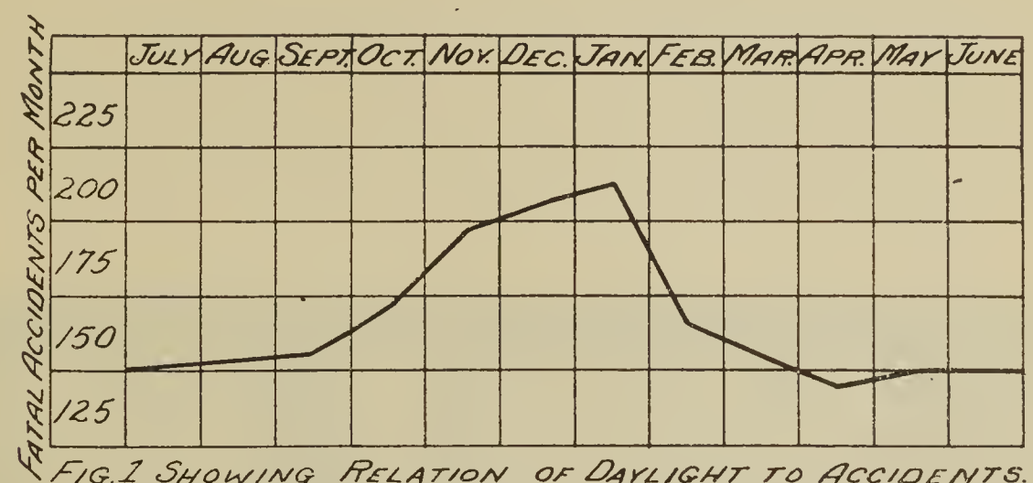

Fig. 1 Showing Relation of Daylight to Accidents.

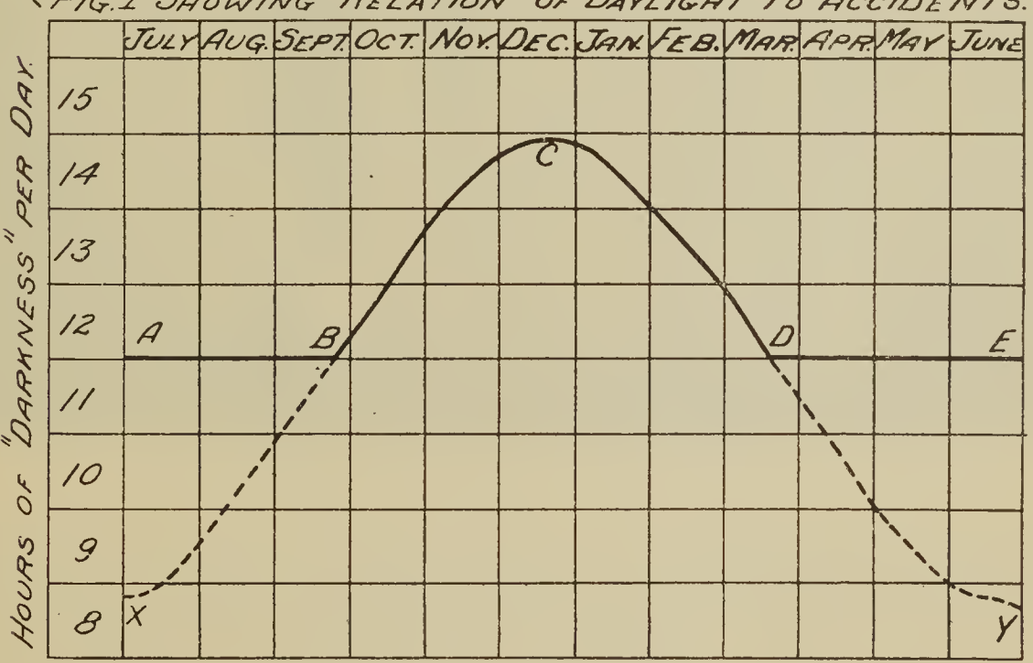

Fig. 2. Distribution of Darkness by Months.

The protection of the workmen's eyesight ought also to be considered. The improper location of lighting units often result in undue eye strain. By improper location we mean unshielded lights so arranged that they are in the direct line of vision, or lights that do not properly illuminate the work. This eye strain often results in headaches, and surely a workman with a headache is unable to do as satisfactory work as when in physically good condition.

Lighting Units.

Tungsten filament lamps* constitute the most recent and important development in high efficiency metal filament lamps. These lamps are made in a range of sizes from 10 to 1,000 watts for multiple operation on 105-125 volt circuits, and from 15 to 500 watts for multiple operation on 220 to 250 volts. The power consumption varies from 1.3 watts per horizontal candle-power, for the smallest size, to 0.60 watts per horizontal candle-power for the largest size. The larger sized lamps are of somewhat different construction from the smaller lamps, since in

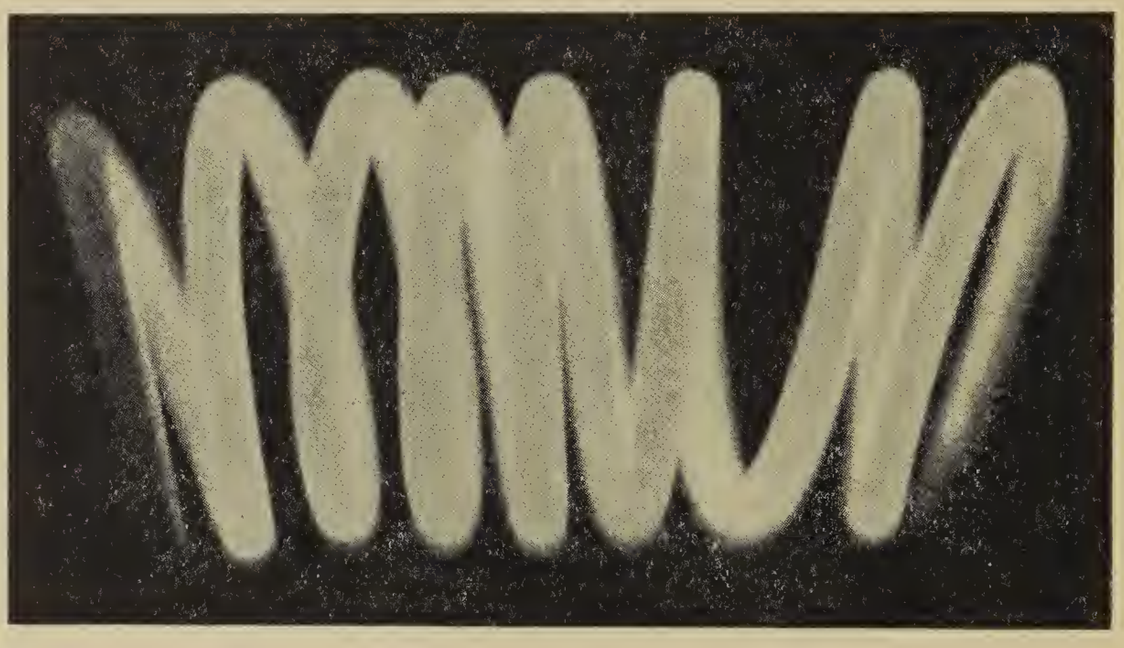

Fig. 3. Section of Filament Enlarged.

the former the filaments are considerably shortened by being coiled into helices. Instead of employing vacua, the bulbs are filled with inert gas of such pressure as to approximate an atmosphere when the lamps are in operation. A view of a section of one of these filaments greatly enlarged is shown in Fig. 3. On account of time available it is obviously impracticable to go into a consideration of the reason for the higher efficiencies of these large sized lamps. For a lengthy discussion of this subject I would refer you to a paper by Irving Langmuir, presented before the A. I. E. E., and which appears in their transactions Vol. XXXII, page 1913.

* Such lamps are designated as MAZDA lamps by all the principal manufacturers in this country.

The distribution of light about a clear bare regular tungsten filament lamp is such that it emits the maximum candlepower perpendicular to the axis of the lamp. This value is known as the mean horizontal candlepower. Fig. 4 shows the distribution of light from clear bare 750 and 1,000 watt tungsten filament lamps. As the greater part of the light received at working points would have to be reflected from the walls, and as the walls are usually dark in this class of work, it is evident that some other means must be provided to redirect the light, in order to assure efficient illumination of the working surfaces.

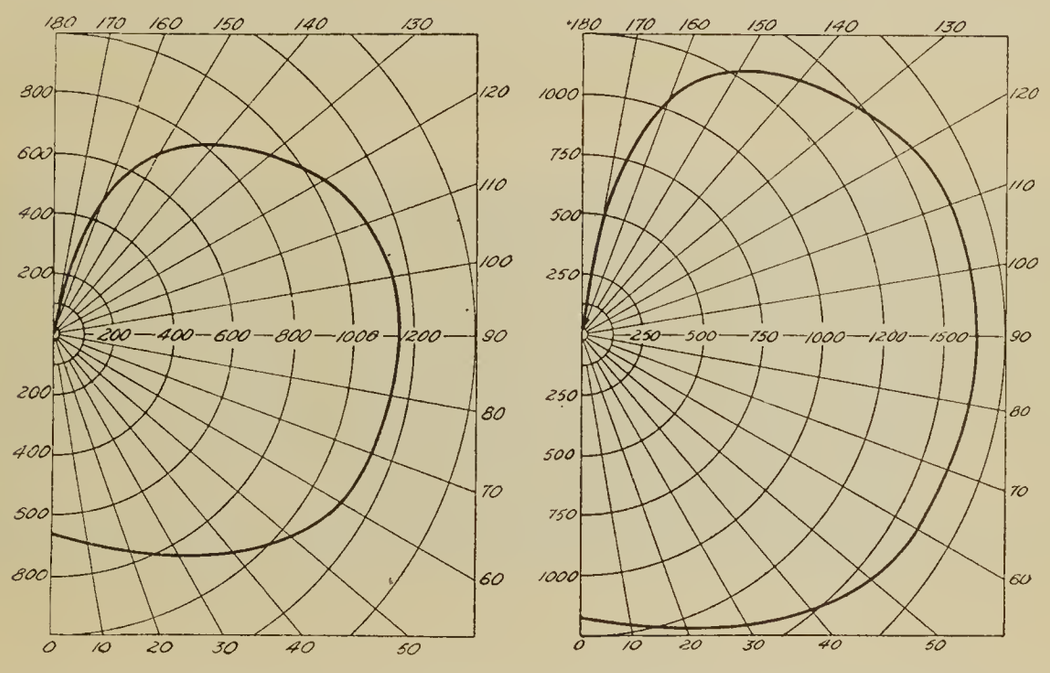

FIG. 4. Distribution from 750 and 1000 Watt Multiple Tungsten Filament Lamps.

This may be accomplished by the use of suitable reflectors, which in addition to this redirecting property, are used to protect the eyes from glare and to diffuse the light.

Reflectors.

Reflectors may be divided into two groups, glass and metal. As the former are not generally as applicable to the lighting of the work under consideration as the steel, we will not consider them.

Aluminum and porcelain enamel are the principal finishes utilized for the reflecting surfaces. The porcelain enamel finish is less susceptible to depreciation, and more readily cleaned. Especially where acid fumes are present this finish is to be preferred.

Enameled steel reflectors are made in a variety of shapes and sizes, thus making it possible to secure a reflector to meet any requirement. The three general shapes are bowl, flat dome and angle.

In Fig. 5 is shown a group of the reflectors above mentioned. The one at the left is typical of the bowl shape. At the right is shown the dome shape. This type is applicable where it is necessary to hang the units at wider spacings than the bowl, since more light is emitted at angles nearer the horizontal. The illumination on the working plane will not be as even as when using the bowl type of reflector, but will be found to be very satisfactory. In the center is shown the angle type. This reflector is used where it is desirable to project the light from

Fig. 5. Typical Porcelain Enameled Steel Reflectors.

one particular direction; for example, in lighting under a ventilating hood. These types of reflectors are obtainable for all sizes of tungsten filament lamps. Knowing the distribution of light, that is, the manner in which the light is reflected, it is possible by correctly spacing and hanging to secure approximately an even illumination over any given area.

Protection from acid fumes should extend to the other accessories. Porcelain sockets should always be used. With open reflectors it is often necessary to protect the lamp base and socket contacts from fumes. A simple means of accomplishing this is to make a gasket of asbestos, which will fit around the neck of the lamp, and press against the inner side of the reflector, thus closing the intervening space. The gasket should be saturated with water-glass before applying.

Mention was previously made regarding the relation of hanging height to spacing. The bowl type steel reflectors are made to give what are known as the extensive, intensive and focusing distributions. The limiting ratio of hanging height to spacing for even illumination with the extensive reflector is 1 to 2; for the intensive 4 to 5 and for the focusing 4 to 3. The flat dome reflector distributes the light over wider angles, and should be spaced from 1½ to 2½ times as far apart as the height above working plane. In Fig. 6 is shown a diagram of the arrangement of units to provide even illumination. The

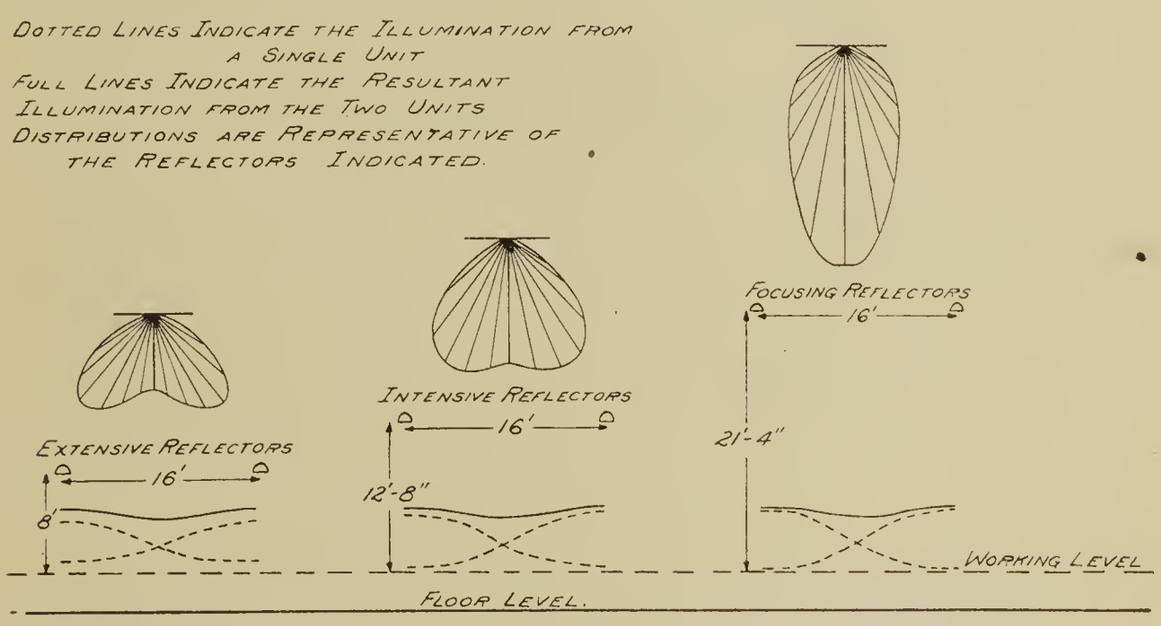

Fig. 6. Diagram showing relation between spacing and hanging height for various types of distribution.

units are spaced at equal distances, the height being varied in accordance with the different distributions.

Methods of Lighting.

There are three general methods of providing light. The direct, the semi-indirect and totally indirect systems of lighting. Obviously the last two systems are not applicable.

Direct lighting may be accomplished by four methods: localized lighting, general illumination, combined localized and general, and localized-general illumination.

Localized lighting consists of the use of small lamps directly under the control of the workmen. Its use is to be avoided as much as possible, as lamp breakage is liable to be high, oper-

ators lose time in adjusting the lighting unit, and glare quite frequently results. There are certain operations where this system may be advisable, such as in the inspection of tanks and electrodes.

In the general system of illumination, medium or large size lamps are used, so hung and spaced as to produce nearly even illumination over the entire area. This system is the one most applicable to the lighting of electrolytic tank rooms, as there are, in general, no places where particularly high intensity is required. Large lamps may be used, thus securing the advantage of their high efficiency. The units are hung high and are

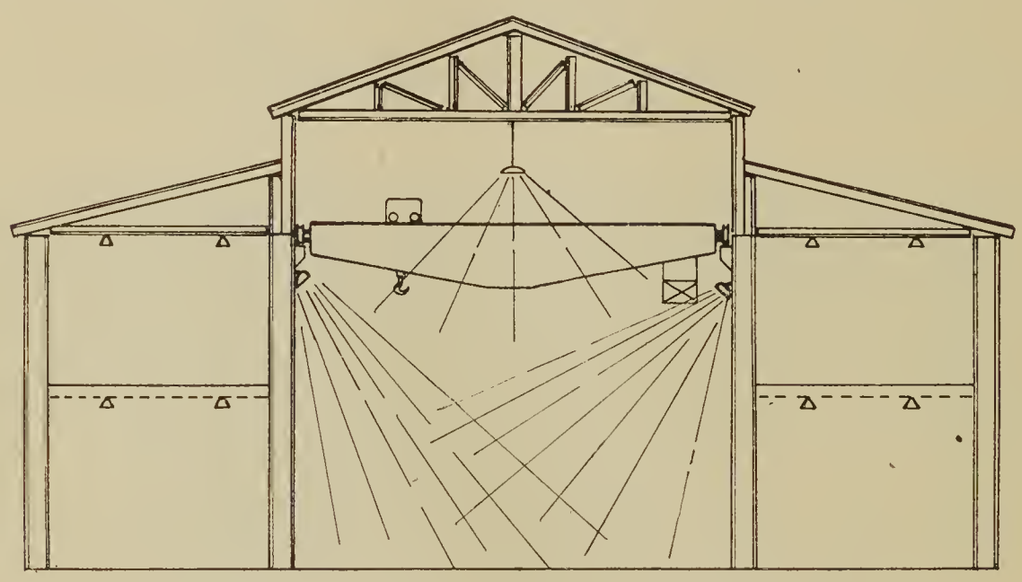

Fig. 7. Diagram of Method of Lighting a Typical Crane Bay Shop.

therefore out of the reach of the workmen, eliminating the liability of breakage due to handling.

In the combined localized and general systems of lighting a low value of illumination is provided by the general system, supplemented by local lights where a higher intensity is required. Although local lamps may be needed at certain points, it is better, if possible, to provide sufficient light by means of general illumination.

The localized-general method of lighting consists of the location of the units with respect to the work at hand. That is, providing a high value of illumination at certain working points. No attempt is made to secure uniform lighting over the entire area. Care must be taken in placing the lighting units in order that the light may come from the proper directions. In large

areas devoted to electrolytic refining, experience has shown that this method is not as applicable as the general system of lighting. Where tanks are used, however, covered by hoods, it has been found that localized lighting is advisable. The method commonly employed is the location of angle reflectors in such a manner as to direct the light from the sides to the tank surfaces.

In Fig. 7 is shown a section of a typical crane bay with the methods of installing lighting units. In the side bays rows of units may be located down the length of the bay. They should be spaced symmetrically and hung at the correct height for the type of reflector selected and spacing distance.

In the central bay is usually found a traveling crane. Two methods of lighting are immediately suggested. One consists of the location of lighting units above the crane. This has the disadvantage that the crane in passing under the lighting units may cause shadows to be cast on the work below. The other consists of the use of angle reflectors located at the sides below the crane on the columns. Cleaning of units and lamp renewals are readily and safely made without interfering with the crane.

Data on Installations.

We will confine the remainder of our discussion to a few specific cases in order to bring out the present lighting practice in this industry.

The buildings used for refining work are usually quite large, nearly all of the floor space being covered by tanks. In some instances these buildings have a high pitched roof with one crane over the entire bay; in others, the building has a lower roof construction with several bays running the total length of the building. Cranes are usually provided for each bay. The tank houses of the Raritan Copper Works, Perth Amboy, N. J., are typical of this last construction.

The roof is of the open-girder type, the building being divided into four bays running the total length, with a traveling crane over each bay. Due to the width of the bays, and the fact that it was impossible to hang angle reflectors at sufficient height on the columns, it was necessary to locate the lighting units on the girders above the cranes.

The lighting units consist of 150-watt clear tungsten filament

lamps. Two rows of units are used for each bay spaced 25 ft. by 35 ft. (7.5 x 10 m.). This makes the wattage consumption 0.17 watts per square foot (1.9 per sq. m.) of floor area. The lamps were hung 19 ft. (6 m.) above the floor and equipped with dome shaped enamel steel reflectors.

A night view of this installation is shown in Fig. 8. This photograph was taken by the light provided entirely by the lamps. It will be noted that the total area of the building is well lighted.

Fig. 8. Night Photograph of Tank House, Raritan Copper Works, Perth Amboy, N. J.

In another plant where refining work was done the construction of the building was somewhat similar to that just noted. For the lighting 250-watt clear tungsten filament lamps were used spaced on 25 ft. (7.5 m.) centers. The units were hung 20 ft. (6 m.) above the floor and equipped with porcelain enamel dome shaped reflectors. The wattage consumption is 0.4 watts per square foot (4.5 per sq. m.). The lighting results are excellent, giving more than twice the illumination obtained in the first case cited.

From data available it is evident that the present practice in

refining plants is the use of clear tungsten filament lamps equipped with dome or bowl shaped enamel steel reflectors. In most cases the wire is run from the panel board to the lamps in conduits. The wattage consumption varies from 0.15 to 0.45 watts per square foot (1.65 to 5 per sq. m.) with an average of about 0.4 (4.5 per sq. m.).

The following instances of the lighting of plating plants will give a good idea of the present practice.

The buildings devoted to this class of work are usually of somewhat different construction, as the areas involved are not as great. In the cases to be cited the buildings were of the closed ceiling type with ceiling heights usually found in this class of plant, *i. e.,* 10 to 14 feet (3 to 4.5 m.).

In one plant 150 watts clear tungsten filament lamps were used spaced 18 ft. by 20 ft., making the wattage consumption 0.42 watts per square foot (4.6 per sq. m.). The lamps were hung 10 ft. (3 m.) above the floor and equipped with dome type enamel steel reflectors. It will be noted that the units were hung closer together in this case than in the previous ones. This was necessary in order to provide fairly even illumination, as the hanging height was lower.

In two other plants devoted to nickel plating, 150-watt clear tungsten filament lamps were used. In one instance they were spaced on 20 ft. (6 m.) centers and in the other 16 ft. by 20 ft. (5 x 6 m.). The corresponding hanging heights were 12 and 10 ft. (3.5 and 3 m.) respectively. The wattage consumption will be found to be 0.38 and 0.47 watts per square foot (4.2 and 5.2 per sq. m.).

From the foregoing it will be seen that the average watts per square foot employed in plating plants is in the vicinity of 0.4 (4.4 per sq. m.). This value is very close to that found in the case of refining plants, indicating this to be a good average value to use for electrolytic tank rooms.

In the summing up it may be well to mention a few of the points brought out. Correct lighting increases safety and production, two factors of vital importance. This correct lighting may be secured by the proper selection of lamps and reflectors, the porcelain enamel reflector being given the preference. Of the various methods of lighting commonly employed, the system

of general illumination is most universally adaptable, although localized-general lighting should be used where tanks are covered by hoods. Considering the question from a cost standpoint, experience has shown that in many cases the cost of proper lighting with the modern lamps is often less than improper lighting with the older types of lamps. In addition the advantages previously mentioned are obtained.

DISCUSSION.

Chairman F. A. Lidbury: The American Electrochemical Society is deeply indebted to the Illuminating Engineering Society for proposing this joint session and for its trouble in providing us this morning with two such interesting and important papers, one on a general and most interesting phase of the subject, and the other a paper of great practical importance. Illuminating engineers are doing very good work in insisting at every opportunity on the connection between good lighting and efficient results in industrial establishments. Few of us connected with industrial operations have failed to be impressed by our own experience in this connection.

At the risk of becoming somewhat unpopular with Mr. Harrington and Mr. Fink, I would call attention to the fact that the relation between the items entering into the cost of lighting is somewhat different in electrolytic installations from that ruling in the majority of cases. In electrolytic plants power is necessarily so cheap that the efficiency of the lamp is of far less consequence than its life. The life of the lamp assumes therefore such importance that it is frequently desirable, particularly in cases where the power is obtained from generating stations whose voltage curves are not always ideal in character, to operate lamps under their rated voltage, giving away efficiency to a certain extent for the sake of obtaining a much longer life.

Lawrence Addicks: I will say a word from the practical side of this subject, having spent a great deal of time in tank houses in general, and this one in particular, under several systems of lighting. Fifteen years ago we had the arc lamps only, which

gave really very unsatisfactory results, due to the corrosion of the mechanism, which could not be kept in proper shape, so that the lights were continually winking. When the mercury vapor lamp came out (and I think the electrolytic people were one of the first to realize the possibilities of that lamp) they were generally installed. I think perhaps that was the best illumination we ever had, from a practical point of view. Of course, we could not use the automatic lamp, as the mechanism which throws it on when you put on the current soon gets out of order. We had to pull a string to start the lamp, and as they were dotted around on the roof, and we could not have the strings hanging down in the room on account of the cranes, it was more or less of a nuisance to start them every time a circuit breaker came out.

The work done at night in a tank house is not of a heavy character; it involves the inspection of contacts, short circuits and things of that sort. The copper itself, being so red in color, made a novel contrast to the greenish light. The room from the outside looked as if there was no light in it. When the tungsten lamps came in they were cheaper, and mercury lamps gave trouble from failure in later years; they did not live as long. When first installed they lasted a long while, but later on we had a good deal of trouble with the lamp, probably because on the manufacturing side the vacuum standard was not properly maintained. The energetic sales propaganda carried on by the tungsten people soon displaced these lamps.

In general, a plant of this kind has one difficulty, the clouding of the glass from moisture and salts, and the old open-arc lamp was free from that objection. The mercury vapor lamp soon frosted over with a film of salt carried up by the moisture. The same with the tungsten lamp. They soon cloud over and we work below the efficiency of the lamp. We are really using frosted lamps after the first day or two.

The greatest gain in lighting in that field has been through the introduction of suitable ventilating apparatus, whereby the evaporation of the liquid is kept down, and the moisture is allowed to escape through proper ventilators, and there is not apparently a rainstorm from the roof. That has enabled us to

paint the roof white, which has made as much advance in the net illumination as has been realized from the technical side.

C. E. Stephens (*Communicated*): The particular points in Mr. Harrington's paper which, to me, seem to predominate, are the great importance of this subject of illumination, and the great variety of phases, any one of which could be made the subject of more extended discussion and much fuller treatment than he has given.

I wish particularly to emphasize the first portion of the paper, in which is given data in such form as will appeal to the management of our industrial and manufacturing establishments. It is no longer necessary to produce scientific papers to convince illuminating engineers of the many advantages of good illumination, but we must bring the matter of proper lighting before the management in such a way that a sufficient appropriation will be provided to cover the expense of the installation. It is now entirely possible, and a very fitting time, to show briefly the advantages of good lighting and the increase in production to be expected, together with the relative cost of the improved service, to our factory executives in such form as will, without question, secure the necessary appropriation.

With a view to furthering this phase of the subject, we will refer to Mr. Harrington's paper, Figs. 1 and 2, showing the relation of daylight to accidents and the distribution of darkness, by months, respectively. It may help some of us the more readily to appreciate the value of sufficient light to note the following features:

Considering average weather conditions throughout a period of one year, note that out of every 24-hour day we have an average of 11¾ hours of darkness, 4½ hours of cloudy or foggy atmosphere, and only 7¾ hours of sunshine. Assuming the average working day to be ten hours, it will be seen that even during the day shift we must operate for a considerable portion of the time by artificial light. In very many plants it is necessary to operate continuously day and night. Then, too, modern processes require to be carried on continuously, and the tremendous investments in plant equipment require that the plant be operated full time to secure greatest economy. Artificial light is, therefore, an absolute necessity.

Numerous data are available which show that the cost of a good lighting system is only a fraction of 1 percent of the gross wages of the employees operating under the lighting system. This gross operating expense does not include the value of the manufacturer's product which was added by manufacturing operation. In the report of the Department of Commerce and Labor, we note that in 1909 the United States had over 360,000 manufacturing establishments employing during the year an average of seven and one-half million persons, of which six and one-half million were actual producers. These establishments paid over four billion dollars in salaries and wages, and turned out product to the value of nearly twenty-one billion dollars, to produce which material costing over twelve billion dollars was consumed. The value of the manufactured product which was added by manufacturing operation was over eight billion dollars.

Numerous estimates have been made which show that the output alone of our plants could be increased from one to eight percent by an adequate lighting system. Assuming that the average increase in output attributable to improved illumination would be 1½ percent (a very conservative figure), the annual saving for all industries in the United States would reach the enormous figure of three hundred and fifteen million dollars, or, over one million dollars per working day.

The 1911 report of the National Electric Light Association's Committee of Industrial Lighting states that from one hundred and sixty-four replies received from manufacturers, thirty-one mention increased production as a result of improving their lighting, and sixty state that the quantity of product has improved and the percentage of seconds decreased.

The census report states that in the year 1909 1 percent of the total product of factories was gross "spoilage," which represents approximately one hundred and fifty million dollars; of this amount 75 percent is estimated to have occurred during periods when working men were using artificial light, and experts seem to agree that at least 25 percent, or over twenty-eight million dollars of this loss, could have been avoided by adequate illumination. Good lighting, therefore, in a modern establishment is cheap at any cost and is an economic necessity.

G. S. Barrows: I would like to express the appreciation of the Illuminating Engineering Society of your invitation to present these papers here. We feel that the Illuminating Engineering Society, which is composed only to a very small extent of illuminating engineers, *per se,* can in this manner get more closely in touch with, and bring the problems of illuminating engineering before other societies in such a way that they will fully appreciate the advantages gained by good illumination. We are working on two lines. We are doing research work, and also purely commercial work, and the two papers which we have had this morning will indicate the lines along which we are working, and will, I hope, be of sufficient interest to you to encourage, perhaps, more papers next year.

G. B. Hogaboom: Artificial lighting of a plating room is a subject which unfortunately has not received much attention and yet it is one of prime importance. The matching of colors is an exceedingly difficult problem even in daylight, and where it must be done under artificial illumination the results are often disappointing.

One of the most trying problems of the plater is to deposit brass so that the color will match a given sample or so as to have the same color on every piece, in order that when the whole article is assembled it will be of a uniform color. If, during the shorter days of the year, inefficient illumination exists and the color of the brass deposit is not up to the standard it is almost useless to try and rectify the trouble, for a brass that appears red under artificial light may be a rich brass color in daylight.

Mr. Barrows spoke of the red wall of the Engineering Building of this institution and the effect it had upon color work being done in an adjoining building. We have experienced much trouble from the same condition. During the time when the sun shone directly on a red-brick building opposite it was useless to try to match samples in the plating room, especially gold or brass ones, as the color was certain to be wrong.

In the plating room the quantity of light is not the essential feature; the color and quality are most important. A subdued light is much preferable, as a strong light is of a great disadvantage when handling highly polished surfaces. This is espe-

cially true of polishing rooms, where a strong reflected light would be injurious to the eyesight of the workmen.

Arc lamps are far from satisfactory, and mercury vapor lamps can not be used on account of the peculiar shade they impart to metals like brass and gold and to green finishes. The tungsten lamp with a frosted globe and with an even distribution of light is now largely used, but the matter of color, that is, reflected color, will give more or less trouble.

W. S. Franklin: I am very much interested to hear what has been said concerning the illumination of the room in which the articles to be seen are highly polished. You no doubt have heard the old statement to the effect that a perfect mirror would be invisible. The only objects which you can see are those from which light is diffusely radiated or reflected. Look at a piece of paper or any object which diffuses light fairly well and you can see it nearly as well if the light comes from a concentrated source as if the light comes from a broad source; but an object which reflects light, like a polished metal object, can not be seen well in a light that comes from a concentrated source. Therefore in a plating establishment, where it is necessary to render polished metal pieces visible, the most important condition is to provide very broad sources of illumination. I should think that indirect illumination would be the most satisfactory in such cases.

G. S. Barrows: I want to call attention to the very great development that is now made in what is known as day-light lighting, that is, we assume a certain value for north daylight, or the north sky, and that is matched by absorbing glass. For different light sources different glasses are required to give average north blue-sky daylight. For an incandescent gas lamp still another glass is necessary. On arc lamps something else may be necessary. The glass can be made absolutely uniform, and we get a light which is better than daylight, because the north light will vary from one season of the year to another season of the year. We have every reason to believe that if we want to do it, and if the expense is justified, we can probably give a glass which, with certain standard lamps, will have no variation at all in the quality of the light. Quite a number of such lamps are now in use, I think particularly in Chicago, nearly every color

printing establishment being now lighted with what is known as daylight lamps. They are not true daylight lamps, as they have only a slight change in the glass, but they give a better light than the ordinary lamp with opal or clear glass globe. While they give a light sufficiently good for most color printing, they are not suitable for the finer color printing.

Now, with the diffusion suggested by Prof. Franklin and daylight glass, which can be obtained to suit any light source, I am very sure that you can get for your color matching a light which would be perfectly satisfactory, and which, because of its uniformity from day to day without reference to the atmospheric conditions, would be more satisfactory even than north daylight.

W. S. Franklin: I wish to make another suggestion. In the reproduction of light which approximates daylight in composition, pale blue glass is used over the lamp. It seems to me there might be cases where tinted paint could be used on the ceiling, so that indirect illumination could be combined with a properly tinted ceiling to give the desired result at once without the interposition of absorbing glasses.

G. S. Barrows: Talking over the matter with Mr. Norman Macbeth, the other day, I find that he is getting away for certain purposes from daylight glass, and is using only monochromatic light.

In the case of a brass plating room it might be possible to make a satisfactory monochromatic light for the illumination of that room. In the case of plating with a somewhat different composition, it might be possible to have another room lighted with another monochromatic light. It is a very simple matter to arrange lighting booths, as they might be called, so that the matching of color of one particular metal could be done in one booth, and the matching of another metal in another booth, the monochromatic light being kept constant throughout the year and of that quality best suited to the particular metal under consideration. With such a light the definition of the metal would be very much more clear than if we simply tried to get one light which would do for every purpose.

C. G. Fink: In reply to Prof. Franklin's suggestion of tinting the ceilings, it is a good one, but the suggestion only applies to

night illumination. You would have to cover up the ceiling in the day time.

G. B. HOGABOOM: Prof. Franklin's remarks about polished surfaces are to the point. On such surfaces the reflection of light is so great that shades are impossible to distinguish. Take two pieces of brass electroplated with cobalt, one plated in a solution containing boric acid, the other in a solution having magnesium sulphate in it. Under artificial light the colors appear identical, while in daylight there is a marked difference. It would appear then, as Mr. Addicks remarked, that it would be necessary to have the same spectrum for the artificial light as you have for daylight.

With a monochromatic light it would be necessary to divide the plating room into units where the different kinds of metal depositing could be carried on. Such a division would not be practical and would be a very expensive proposition.

LAWRENCE ADDICKS: Practically all of this discussion on the matching of colors is a question of the spectrum of the light in which we are dealing. Mr. Hogaboom said he could not match brass. Of course, he did match the brass for the particular light. The only trouble was he did not use a light emitting a spectrum which is standard.

That brings up the question of daylight, and the illuminating engineer is trying to lead us into the idea that we should use some other composition than daylight part of the time. I think it is better to match colors either by daylight, or under a light of the same spectrum, as we are eventually going to have 24-hour daylight artificially.

W. R. MOTT: Relative to the remarks of Mr. Hogaboom I suggest that he could detect the difference between those plates in the light of a snow-white flame arc.

Relative to the snow-white flame arc, which is a light about the whiteness of the blue of a north sky, it is interesting to remark in this connection that photo-engravers find that light suitable for color-process work. Color-process work calls for a very uniform and steady illumination of constant value, and I believe that these lights are constant within ten percent of the actual amount of light emitted under good, reasonable operation,

and that the composition hardly varies at all. Further, the efficiency is at least five times as great as that of the nitrogen-filled lamp for equal power on the circuit, and on alternating current is somewhat greater. It has also displaced practically all of the mercury arcs for the photo-engraving field.

CHAIRMAN LIDBURY: I would like to ask some of the tungsten specialists here what the efficiency of the nitrogen-filled lamp becomes when it is employed with a suitable filter for giving the same values as daylight?

R. E. HARRINGTON: There are three general types of color matching units for use with high efficiency tungsten lamps with which I am familiar:

First, that for accurate color matching.

Second, so-called noon sunlight of less accuracy than the first.

Third, afternoon sunlight; this latter is less efficient than the second type.

Assuming that a high-efficiency tungsten filament lamp is used operating at 0.6 watt per mean horizontal c. p., the power consumption, using the second type of color-matching unit, will be in the vicinity of 1.25 watts per candle. Of course the nearer the approach to accurate color-matching light the less the efficiency or, in other words, an increase numerically in the watts per candle.

Regarding Prof. Franklin's question concerning a tinted ceiling, it would be necessary that a ceiling of this nature be of a matte surface. This is necessary in order to reduce glare and optical fatigue. Such a surface of course will absorb more or less light. In addition tinting the ceiling will introduce a certain percentage of absorption, depending on the amount of tinting required. There is a question whether the tinted ceiling is, from an efficiency standpoint, better than using some type of absorbing screen around the lamp.

Concerning the point that Mr. Addicks brought up regarding the selection of light that has the true value of daylight, and using that for color matching, the question will come up again, as it has in previous instances, of what will be selected as daylight. It is recognized that the quality of daylight is quite variable from morning to night.

An instance came to my attention some time ago of color matching in a celluloid plant. There are several grades of whiteness of celluloid ranging from yellow to white and it is found for the color matching in this particular plant that there were approximately two hours per day during which it was possible to match the celluloid, and as soon as these two hours were up the color matchers had to quit work. If you select for this particular plant a color of light that approaches that received during these two hours you have selected the proper color to meet their conditions. Doubtless at other plants where color matching has to be done conditions similar to these will be found.

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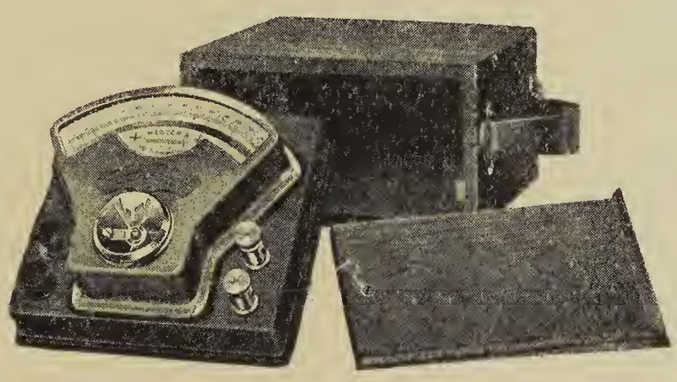

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A full description of Model 1 Voltmeters will be found in Bulletin No. 501, which will be mailed on request.

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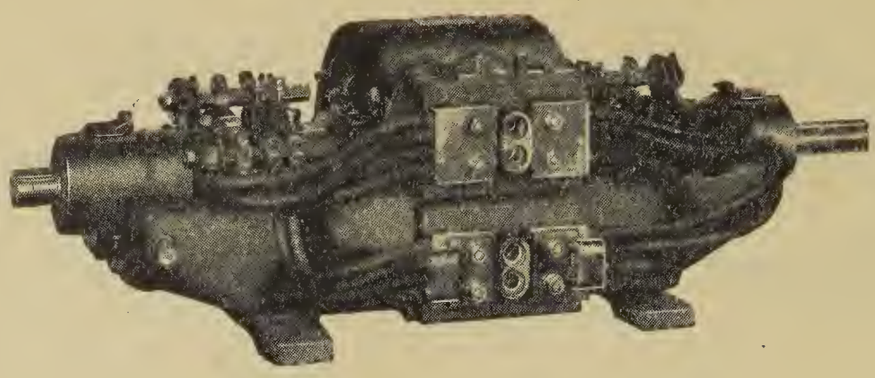

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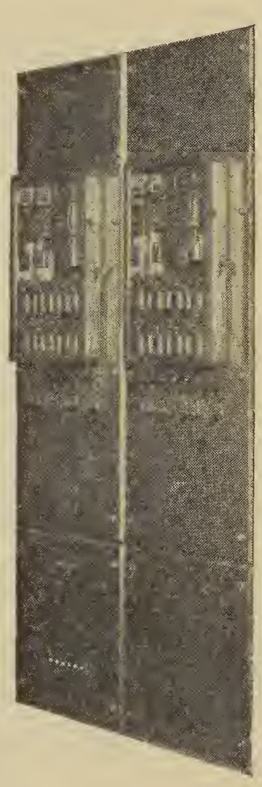

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